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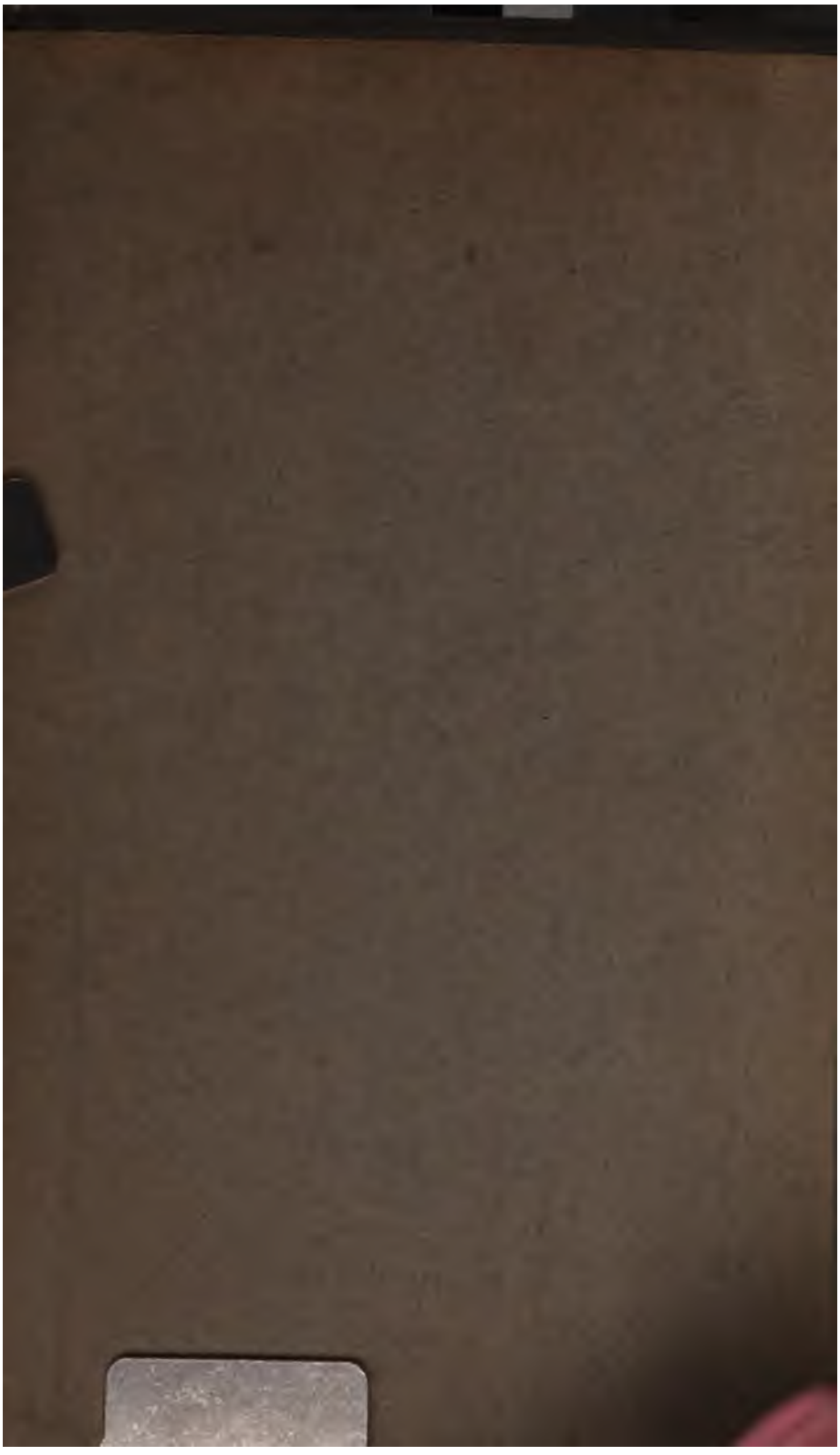

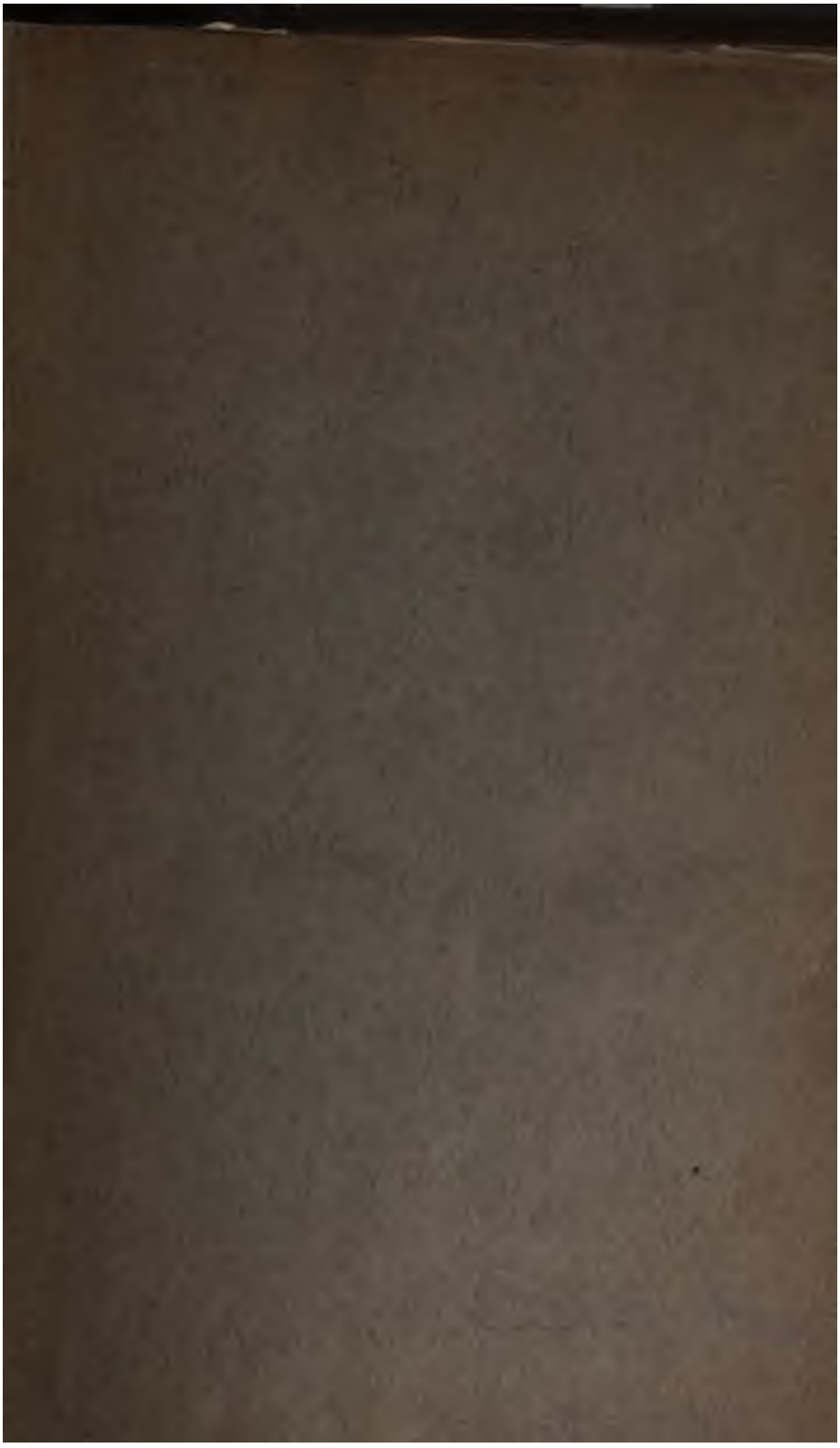

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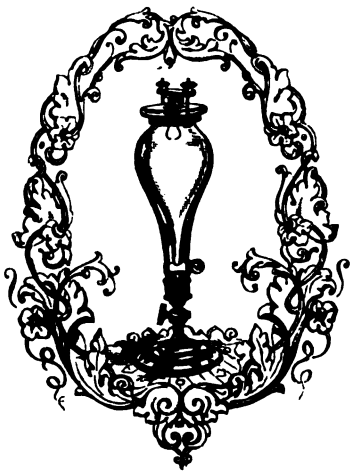

FOUNDED 1846.

HAND-BOOK

OF

CHEMISTRY.

BY

LEOPOLD GMELIN,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF HEIDELBERG.
AND MEMBER OF VARIOUS LEARNED SOCIETIES IN BERLIN, BONN, CATANIA, DRESDEN, FREIBURG, FRANKFORT, GÖTTINGEN, HALLE, HAMBURG, HANAU, HEIDELBERG, JASSY, LONDON, MARBURG, MUNICH, PARIS, PETERSBURGH, VIENNA, AND WETTERAU.

NEW YORK
PUBLIC

VOL. I.

COHESION, ADHESION, AFFINITY, LIGHT, HEAT, AND ELECTRICITY.

TRANSLATED BY

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LONDON:
PRINTED FOR THE CAVENDISH SOCIETY.

MDCCCXLVIII.

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TRANSLATOR'S PREFACE.

THE volume now offered to the members of the Cavendish Society is the first part of a translation of Gmelin's "*Handbuch der Chemie*," comprising the General Laws of Chemical Action, and the Chemical Relations of Light, Heat, and Electricity. The publication of the last edition of this Great Standard Work was commenced by the author in 1843,—since which time, these branches of science have been enriched by many important discoveries. A full account of the whole of these researches would have extended the volume to too great a length; I have therefore contented myself with introducing the most important. The principal additions relate to the following subjects;—Relation between Atomic Weight and Density;—Relation of Light to Magnetism; the Calotype Process; Thermography;—Radiation and Conduction of Heat; Expansion; Specific Heat; Latent Heat of Liquids and of Vapours; Tension of Vapours; Liquefaction and Solidification of Gases; Development of Heat in Chemical Combination; Decomposition of Water by Heat;—Development of Electricity by the escape of High-pressure steam; Grove's Gas Voltaic Battery; and the Magnetic Condition of all Matter.—Additions have likewise been made to the lists of Memoirs at the heads of the chapters. The new matter is kept quite distinct from the original; more complete incorporation would have required alterations in the text, which a translator is by no means justified in making.

A few words are necessary with regard to nomenclature. In the portion of the work included in the present volume,—relating principally to physical science,—it has been the Author's practice rather to copy or translate the terms used by the different writers from whose works or memoirs he has borrowed, than to adopt a strictly systematic nomenclature. A similar course is, for the most part, pursued in the translation,—retaining, for example, the ordinary terms, *sulphuret* and *phosphuret*, instead of the more systematic appellations, *sulphide* and *phosphide*, proposed by Professors Graham and Hofmann. It is true that this mode of pro-

ceeding renders the nomenclature adopted in the present volume somewhat different from that which will be employed in the sequel: but the differences thereby occasioned are not likely to create confusion, especially as the nomenclature to be used in the remainder of the work will be fully explained in the course of the second volume.

The names of several of the elements in the original are somewhat different from those in common use; for instance, the ordinary terms *Magnesium*, *Aluminum*, and *Glucinum*, are, for the sake of brevity, replaced by *Magnium*, *Alumium*, and *Glycium*. These alterations it is impossible to retain in an English translation; for the adoption of them would render it necessary to substitute the corresponding terms *Magnia*, *Alumia*, and *Glycia*, for *Magnesia*, *Alumina*, and *Glucina*,—an alteration which we are scarcely at liberty to make, especially with words of such common occurrence as *magnesia* and *alumina*. In German, the same difficulty does not occur: for the names of the three oxides in question are totally different in form from those of the corresponding metals, viz. *Talkerde* for magnesia, *Thonerde* for alumina, and *Beryllerde* for glucina.

The decimal weights and measures employed in the original have been retained in the translation. If it should be thought necessary, in any particular instance, to ascertain the equivalent values in the English system, the required data will be found in a table near the beginning of the work (p. ix). For the most part, however, such reductions may be entirely dispensed with: for scientific chemistry is more concerned with relative than with absolute magnitudes; and therefore, the particular unit or mode of subdivision adopted is unimportant, except in so far as convenience and simplicity are concerned; and in these respects, the decimal system is incomparably superior to every other. In some few instances, in which absolute magnitudes are of special importance, the English equivalents are given in addition to the original data in the decimal system.

H. W.

University College,
December, 1848.

LIST OF ABBREVIATIONS USED IN THIS WORK.

Crell, chem. J. signifies: Chemisches Journal, von *Dr. Lorenz Crell.* Lemgo. 1778—1781. 6 Parts.

Crell, N. Entd.—Die neuesten Entdeckungen in der Chemie, von *Dr. Lorenz Crell.* Leipzig. 1781—1784. 12 Parts.

Crell, Ann.—Chemische Annalen, von *Dr. Lorenz Crell.* Hemst and Leipzig. 1784—1804. 40 Volumes.

Voigt N. Mag.—Magazin für den neuesten Zustand der Naturkunde, von *Joh. Heinr. Voigt.* Jena, Weimar. 1797—1806. 12 Vol.

Gren, A. J.—Journal der Physik, von *F. A. C. Gren.* Halle and Leipzig. 1790—1794. 8 Vol.

Gren, N. J.—Neues Journal der Physik, von *F. A. C. Gren.* Leipzig. 1795–97. 4 Vol.

Gilb.—Annalen der Physik; edited by *L. W. Gilbert.* Halle. 1799—1824. 76 Vol.

Pogg.—Annalen der Physik und Chemie, von *Poggendorff.* Leipzig. 1824—1827. 72 Vol.

Scher. J.—Allgemeines Journal der Chemie; edited by *Dr. Al. Nic. Scherer.* Leipzig. 1799—1803. 10 Vol.

Scher. N. Bel.—Nordische Blätter für die Chemie, von *Al. Nic. Scherer.* Halle. 1817. 1 Vol.

Scher. N. Ann.—Allgemeine Nordische Annalen für die Chemie, von *Al. Nic. Scherer.* Petersburg. 1819—1822. 8 Vol.

A. Gehl.—Neues allgemeines Journal der Chemie; edited by *A. F. Gehlen.* Berlin. 1803—1805, 6 Vol.

N. Gehl.—Journal für die Chemie und Physik; edited by Dr. *A. F. Gehlen.* Berlin; also, Journal für die Chemie, Physik, und Mineralogie; edited by Dr. *A. F. Gehlen.* Berlin. 1806—1810. 9 Vol.

Schw.—Journal für Chemie und Physik; edited by Dr. *J. S. C. Schweigger.* Nürnberg, Halle. 1811—1833. 69 Vol.

J. techn. Chem.—Journal für technische und ökonomische Chemie, von *O. L. Erdman.* 1828–33. 18 Vol.

J. pr. Chem.—Journal für praktische Chemie von *O. L. Erdmann*, up to 1836 with Schweigger-Seiddel, after 1839 with R. F. Marchand. 1834–47. 42 Vol. *Continued.*

A. Tr.—Journal der Pharmacie, von *Joh. Barthol. Trommsdorff.* Leipzig. 1794—1816. 25 Vol.

N. Tr.—Neues Journal der Pharmacie, von. *Joh. Barthol. Trommsdorff.* Leipzig. 1817–34. 27 Vol.

Taschenb.—Taschenbuch für Scheidekünstler und Apotheker. Weimar. 1780—1829. 50 Vol.

Berl. Jahrb.—Berlinisches Jahrbuch der Pharmacie. Berlin. 1795—1841. 45 Vol. *Continued.*

Repert.—Repertorium für die Pharmacie, von Buchner (the first volume by *Gehlen*). Erlangen. 1815–42. 76 Vol. *Continued.*

Br. Arch.—Archiv. des Apothekervereins im nördlichen Deutschland, von *Rud. Brandes.* 1822–31. 39 Vol.

N. Br. Arch.—Archiv. der Pharmacie des Apothekervereins im nördlichen Deutschland, von *Rud. Brandes.* Second Series. 1835—1842. 32 Vol. *Continued.*

Mag. Pharm.—Magazin der Pharmacie; edited first by *Hänle*, afterwards by *Geiger*. Karlsruhe. 1823–31. 36 Vol.

Ann. Pharm.—Annalen der Pharmacie; by *Liebig*, and occasionally also by *Geiger, Brandes, Trommsdorff, Merk, Mohr;* since 1838 compiled by Liebig and Wöhler, and since 1840, together with Vol. 33, under the title: Annalen der Chemie und Pharmacie von *Frederich Wöhler* und *Justus Liebig*. Altogether from 1832—1847. 64 Vol. *Continued.*

Kastn. Archiv.—Archiv. für die gesammte Naturlehre, von *K. W. G. Kastner*. Erlangen. From 1830, together with the 19th Vol., under the title: Archiv. für Chemie und Meteorologie, von *K. W. G. Kastner*. Erlangen. Altogether from 1824—1835. 27 Vol.

Zeitschr. Phys. Math.—Zeitschrift für Physik und Mathematik, von *Baumgartner* und *Ettinghausen*. Wien. 1826–31. 10 Vol.

Zeitschr. Phys. v. W.—Zeitschrift für Physik und verwandte Wissenschaften, von *Baumgarten* (since 1837 by *Holger*). Wien. 1832—1840. 6 Vol. *Continued.*

J. Phys.—Journal de Physique, de Chimie, d'Histoire Naturelle et des Arts. Par *Rozier,—Delametherie,—Ducrotay de Blainville*. Paris. 1771—1823. 96 Vol.

Mem. d'Arcueil.—Mémoires de Physique et de Chimie de la Société d'Arcueil. Paris. 1807–17. 3 Vol.

Ann. Chim.—Annales de Chimie, ou Recueil de Mémoires concernant la Chimie et les Arts qui en dependent, et spécialement la Pharmacie. Paris. 1781—1815. 96 Vol.

Ann. Chim. Phys.—Annales de Chimie et Physique. Par MM. *Gay-Lussac* et *Arago*. Paris. 1816–40. 75 Vol.

N. Ann. Chim. Phys.—Annales de Chimie et Physique, par *Gay-Lussac, Arago, Dumas, Pelouze, Boussingault*, et *Regnault*. Troisième Série. Paris. 1841–47. 21 Vol. *Continued.*

J. Polyt.—*Journal de l'Ecole Polytechnique*. Paris. 1797. 22 Parts.

Ann. du Mus.—Annales du Muséum d'Histoire Naturelle. Paris. 1802—1813. 20 Vol.

Mém. du Mus..—Mémoires du Muséum d'Histoire Naturelle. Paris. 1815–32. 20 Vol.

N. Ann. du Mus.—Nouvelles Annales du Musée d'Histoire Naturelle. 1832–35. 4 Vol.

Bibl. brit.—Bibliothèque britannique, Sciences et Arts. Genève. 1796—1815. 60 Vol.

Bibl. univ.—Bibliothèque universelle. Sciences et Arts. Genève. 1816–35. 60 Vol.

N. Bibl. univ.—Bibliothèque universelle de Genève. Nouvelle Série. 1836–42. 42 Vol.

Bull. philom.—Bulletin (and Nouveau Bulletin) des Sciences, par la Société philomatique de Paris.

J. Mines.—Journal des Mines. Paris. 1794—1815. 38 Vol.

Ann. Mines.—Annales des Mines. Paris. Première Série. 1816–26. 13 Vol.—Deuxième Série. 1827–30. 8 Vol.—Troisième Série. 1832–41. 20 Vol.—Quatrième Série. 1842. 2 Vol.

Bull. Pharm.—Bulletin de Pharmacie, par *Cadet, Planche, Boullay*, &c. Paris. 1809–14. 6 Vol.

J. Pharm.—Journal de Pharmacie. 1815–42. 29 Vol. *Continued.*

J. chim. med.—Journal de chimie médicale, de pharmacie, et de toxicologie. Paris. 1825–42. 18 Vol. *Continued.*

Ann. Sc. nat.—Annales des Sciences naturelles, par Audoin, Brogniart, et Dumas. 1824–33. 30 Vol. *Continued.*

N. Ann. Sc. nat. Bot.—Annales des Sciences naturelles, etc. Seconde Série. Botanique. 1834–42. 18 Vol. *Continued.*

N. Ann. Sc. nat. Zool.—Annales des Sciences naturelles, etc. Seconde Série. Zoologie. 1834–42. 18 Vol. *Continued.*

Compt. rend.—Comptes rendus hebdomadaires des Séances de l'Academie des Sciences. Paris. 1835–42. 15 Vol.

Phil. Trans.—Philosophical Transactions of the Royal Society of London. London. 1665—1847. *Continued.*

Phil. Mag.—Philosophical Magazine and Journal, by *Tilloch* (and *Taylor*). London. 1798—1826. 68 Vol.

Ann. Phil.—Annals of Philosophy. London. The first 16 volumes up to 1820, by *Thomas Thomson;* the following 12, as a New Series, by *Richard Phillips.* Altogether from 1818 to 1826. 28 Vol.

Phil. Mag. Ann.—The Philosophical Magazine and Annals. By *Richard Taylor* and *Richard Phillips.* 1827–32. 11 Vol.

Phil. Mag. J.—The London and Edinburgh Philosophical Magazine and Journal of Science, by *Brewster, Taylor,* and *R. Phillips.* 1832–47. 31 Vol. *Continued.*

Quart. J. of Sc.—The Quarterly Journal of Science, Literature, and Art. London. 1816–27. 22 Vol.

N. Quart. J. of Sc.—The Quarterly Journal of Science, Literature, and Art. New Series. London. 1327–30. 7 Vol.

J. Roy. Inst.—The Journal of the Royal Institution of Great Britain. London. 1830–31. 2½ Vol.

Edinb. J. of Sc.—The Edinburgh Journal of Science; by *David Brewster.* Edinburgh and London. 1824–29. 10 Vol.

Edinb. Phil. J.—The Edinburgh Philosophical Journal; by *Robert Jameson* (up to 1824 also by *David Brewster*). Edinburgh. 1819—1826. 14 Vol.

N. Edinb. Phil. J.—The Edinburgh New Philosophical Journal, by *Robert Jameson.* Edinburgh. 1826–47. 43 Vol. *Continued.*

Sill. Am. J.—The American Journal of Science and Arts; by Silliman. Newhaven. 1819–45. 49 Vol. Second Series, Vol. 1—3. *Continued.*

Brugn. Giorn.—Giornale di fisica, chimica, e storia naturale, di *Luigi* (latterly by *Gaspari*) *Brugnatelli.* Pavia. 1808–26. 19 Vol.

Bibl. ital.—Bibliotheca italiana. Milano. 1816–40. 100 Vol.

Bergman. Opusc.—*Torberni Bergman:* Opuscula physica et chemica. Holm, Ups. et Aboæ. 1779–90. 6 Vol.

Scheele Opusc.—*Car. Guil. Scheele:* Opuscula chemica et physica. Lips. 1788—1789. 2 Vol.

Klaproth Beitr.—Beiträge zur chemischen Kenntniss der Mineral-körper, von *M. H. Klaproth.* Berl. u. Stett. 1795—1815. 6 Vol.

Dalton, System.—A new System of the Chemical part of Natural Philosophy, by *John Dalton.* Manchester. 1808. 2 Vol.

Davy, Elem.—Elements of the Chemical part of Natural Philosophy, by *Sir Humphry Davy.* London. 1810.

Gay-Lussac et Thénard, Recherch.—Recherches physico-chimiques, par *Gay-Lussac et Thénard.* Paris. 1811. 2 Vol.

Berzelius Jahresb.—Jahresbericht über die Fortschritte der physischen Wissenschaften, von *Jacob Berzelius.* Tubingen. 1822–47. 26 Vol.

Berzelius Lehrb.—Lehrbuch der Chemie, von *J. J. Berzelius.* Dritte Auflage. Dresden und Leipzig. 1833–41. 10 Vol.

Mitscherlich Lehrb.—Lehrbuch der Chemie, von *E. Mitscherlich. Aufl.* 2. Berlin. 1834–40. 2 Vol.

Graham Elements.—Elements of Chemistry, by *Thomas Graham.* London. 1842.

Graham Lehrb.—A translation of the same into German, by F. J. Otto. Brunswick. 1840–41. 2 Vol.

H. Rose. Anal. Chem.—Handbuch der analytischen Chemie, von *Heinrich Rose.* Aufl. 4. Berlin. 1838. 2 Vol.

Dumas angew. Chem.—Handbuch der angewandten Chemie, von *J. Dumas:* übers. von G. A. und Fr. Engelhart. Nürnberg. 1830–37. Bis jetzt. 5 Bände.

All temperatures are given in degrees of the Centigrade thermometer —excepting when otherwise expressly stated.

The names of authors who have made their investigations in concert are connected by &, not by *and.*

All sections, paragraphs, &c., added by the Translator are distinguished by the sign ¶ at the beginning and end; additional footnotes are signed [W].

WEIGHTS AND MEASURES.

In the new French system of weights and measures, a Metre is the ten-millionth part of the distance from the North Pole to the Equator, or of half the length of a meridian. It is divided into tenths, hundredths, and thousandths, or Decimetres, Centimetres, and Millimetres.

1 Metre = 0·513074 French Toises = 3 Paris Feet and 11·1 Lines = 36·94128 Par. Inches = 39·37079 English Inches.—A French Foot = 0·32484 met.; an English Foot = 0·3047946 met., and a Swedish Foot = 0·296867 met.

1 Cubic Metre = 1 Stère = 1000 Litres = 1,000,000 Cubic Centimetres.

1 Cubic Decimetre = 1 Litre = 1000 Cubic Centimetres.

1 Gallon English = 4·543 Litres.

1 Cubic Centimetre of water at + 4° C., its point of maximum density, weighs 1 Gramme: hence, 1 Litre of water at 4° weighs 1000 Grammes (about 2 pounds); and 1 Stère of water weighs 1,000,000 Grammes = 1000 Kilogrammes.

10,000 Grammes = 1 Myriagramme; 1000 Grammes = 1 Kilogramme; 100 Grammes = 1 Hectogramme; 10 Grammes = 1 Decagramme; 0·1 Gramme = 1 Decigramme; 0·01 Gramme = 1 Centigramme; 0·001 Gramme = 1 Milligramme.

1 Gramme = 18·82715 Fr. grains, poids de marc (72 grains = 1 dram); = 16·091022755 grains, Nüremberg weight; = 281·01569 Richtpfennigtheilchen, Kölnish Markgewicht (65536 Richtpfennigtheilchen = 8 ounces or 1 mark); = 0·56475 drams, English avoirdupois (16 drams = 1 ounce, 16 ounces = 1 pound); = 15·44242 grains, English troy imperial (480 gr. = 1 oz. 12 oz. = 1 lb.); = 0·23505 Solotnik, Russian weight (3 Solotnik = 1 Loth, 32 Loth = 1 pound); = 22·54086 Doli (96 Doli = 1 Solotnik, 288 Doli = 1 Loth, and 9216 Doli = 1 Russian pound).

1 Paris Cubic Inch of water at 4° weighs 19·836 Grammes = 319·4 Grains Nüremberg weight;—1 Rhenish Cubic Inch of water weighs 17·891 Grammes = 288·1 Nür.;—1 English Cubic Inch of water weighs 16·891 Grammes = 264·5 Nür. wt.

1 Apothecaries' pound (12 oz.) weighs: in Austria, 420·009 Grammes —in Holland, 374·96 grm.—in England, troy-weight, 372·9986 grm.—in Bavaria, 360 grm.—in Nüremberg, 357·66391 grm.—in Hanover, 357·56686 grm.—in Sweden, 356·22687 grm.—in Prussia, 350·78348 grm.

Areometer for Liquids heavier than Water.

Deg.	Beck.	Baumé.		Deg.	Beck.	Baumé.		Deg.	Beck.	Baumé.	
		a.	*b.*			*a.*	*b.*			*a.*	*b.*
1	1·0059	1·008	1·007	26	1·1806	1·220	1·215	51	1·4286	1·546	1·531
2	1·0119	1·015	1·014	27	1·1888	1·230	1·225	52	1·4407	1·563	1·546
3	1·0180	1·022	1·020	28	1·1972	1·241	1·235	53	1·4530	1·580	1·562
4	1·0241	1·029	1·028	29	1·2057	1·252	1·245	54	1·4655	1·598	1·578
5	1·0303	1·036	1·034	30	1·2143	1·263	1·256	55	1·4783	1·616	1·596
6	1·0366	1·043	1·041	31	1·2230	1·274	1·267	26	1·4912	1·634	1·615
7	1·0429	1·051	1·049	32	1·2319	1·285	1·278	57	1·5044	1·653	1·634
8	1·0494	1·059	1·057	33	1·2409	1·296	1·289	58	1·5179	1·672	1·653
9	1·0559	1·067	1·064	34	1·2500	1·308	1·300	59	1·5315	1·691	1·671
10	1·0625	1·075	1·072	35	1·2593	1·320	1·312	60	1·5454	1·711	1·690
11	1·0692	1·083	1·080	36	1·2687	1·332	1·324	61	1·5596	1·732	1·709
12	1·0759	1·091	1·088	37	1·2782	1·345	1·337	62	1·5741	1·753	1·729
13	1·0828	1·099	1·096	38	1·2879	1·358	1·349	63	1·5888	1·775	1·750
14	1·0897	1·107	1·104	39	1·2977	1·371	1·361	64	1·6038	1·797	1·771
15	1·0968	1·116	1·113	40	1·3077	1·384	1·375	65	1·6190	1·819	1·793
16	1·1039	1·125	1·121	41	1·3178	1·397	1·388	66	1·6346	1·842	1·815
17	1·1111	1·134	1·130	42	1·3281	1·410	1·401	67	1·6505	1·866	1·839
18	1·1184	1·145	1·138	43	1·3386	1·424	1·414	68	1·6667	1·891	1·864
19	1·1258	1·152	1·147	44	1·3492	1·438	1·428	69	1·6832	1·916	1·885
20	1·1333	1·161	1·157	45	1·3600	1·453	1·442	70	1·7000	1·942	1·909
21	1·1409	1·170	1·166	46	1·3710	1·468	1·456	71		1·968	1·935
22	1·1486	1·180	1·176	47	1·3821	1·483	1·470	72		1·995	1·960
23	1·1565	1·190	1·183	48	1·3934	1·498	1·485	73		2·023	
24	1·1644	1·200	1·195	49	1·4050	1·514	1·500	74		2·052	
25	1·1724	1·210	1·205	50	1·4167	1·530	1·515	75		2·081	

The scales of Beck, Cartier, *b*, and Beaumé *b*, are taken from Graham's *Lehrbuch*, I, 158; those of Cartier *a* and Beaumé *a*, in which the specific gravity of water at 12·5° C. is assumed = 1·000, and likewise the scale of Gay-Lussac's Alcoholometer, are from Maroseau's Memoir. (*J. Pharm.* 16, 482.)

Areometer for Liquids lighter than Water.

Deg.	Beck.	Cartier.		Baumé.	Deg.	Beck.	Cartier.		Baumé.
		a.	*b.*				*a.*	*b.*	
70	0·7083				55	0·7556	..	..	0·763
69	0·7112				54	0·7589			
68	0·7142				53	0·7623			
67	0·7173				52	0·7658			
66	0·7203				51	0·7692			
65	0·7234				50	0·7727	..	..	0·784
64	0·7265				49	0·7763	..	..	0·788
63	0·7296				48	0·7799	..	..	0·792
62	0·7328				47	0·7834	..	..	0·795
61	0·7359				46	0·7871	..	..	0·799
60	0·7391	..	..	0·744	45	0·7907	..	..	0·803
59	0·7423				44	0·7944	0·794	..	0·807
58	0·7456				43	0·7981	0·799	..	0·811
57	0·7489				42	0·8018	0·804	..	0·816
56	0·7522				41	0·8061	0·809	..	0·820

Deg.	Beck.	Cartier.		Baumé.	Deg.	Beck.	Cartier.		Baumé.
		a.	*b.*				*a.*	*b.*	
40	0·8095	0·814	..	0·824	20	0·8947	0·929	0·934	0·933
39	0·8133	0·819	0·824	0·829	19	0·8994	0·935	0·941	0·939
38	0·8173	0·825	0·829	0·834	18	0·9042	0·942	0·948	0·946
37	0·8212	0·830	0·834	0·839	17	0·9090	0·949	0·955	0·952
36	0·8252	0·835	0·839	0·844	16	0·9139	0·956	0·962	0·959
35	0·8292	0·840	0·845	0·849	15	0·9189	0·963	0·969	0·965
34	0·8333	0·845	0·850	0·854	14	0·9239	0·970	0·976	0·972
33	0·8374	0·851	0·855	0·859	13	0·9289	0·977	..	0·979
32	0·8415	0·856	0·861	0·864	12	0·9340	0·985	..	0·986
31	0·8457	0·862	0·866	0·869	11	0·9392	0·992	..	0·992
30	0·8500	0·867	0·872	0·875	10	0·9444	1·000	..	1·000
29	0·8542	0·872	0·878	0·881	9	0·9497			
28	0·8585	0·879	0·883	0·886	8	0·9550			
27	0·8629	0·885	0·889	0·892	7	0·9604			
26	0·8673	0·891	0·895	0·897	6	0·9659			
25	0·8717	0·897	0·901	0·903	5	0·9714			
24	0·8762	0·903	0·907	0·909	4	0·9770			
23	0·8808	0·909	0·914	0·915	3	0·9826			
22	0·8854	0·916	0·921	0·921	2	0·9883			
21	0·8900	0·922	0·927	0·927	1	0·9941			

Gay-Lussac's Alcoholometer (Alcoomètre) at 15°.

Degree.	Sp. Gr.	Degree.	Sp. Gr.	Degree.	Sp. Gr.	Degree.	Sp. Gr.
100	0·795	75	0·879	50	0·936	25	0·971
99	0·800	74	0·881	49	0·938	24	0·972
98	0·805	73	0·884	48	0·940	23	0·973
97	0·810	72	0·886	47	0·941	22	0·974
96	0·814	71	0·888	46	0·943	21	0·975
95	0·818	70	0·891	45	0·945	20	0·976
94	0·822	69	0·893	44	0·946	19	0·977
93	0·826	68	0·896	43	0·948	18	0·978
92	0·829	67	0·899	42	0·949	17	0·979
91	0·832	66	0·902	41	0·951	16	0·980
90	0·835	65	0·904	40	0·953	15	0·981
89	0·838	64	0·906	39	0·954	14	0·982
88	0·842	63	0·909	38	0·956	13	0·983
87	0·845	62	0·911	37	0·957	12	0·984
86	0·848	61	0·913	36	0·959	11	0·986
85	0·851	60	0·915	35	0·960	10	0·987
84	0·854	59	0·918	34	0·962	9	0·988
83	0·857	58	0·920	33	0·963	8	0·989
82	0·860	57	0·922	32	0·964	7	0·990
81	0·863	56	0·924	31	0·965	6	0·992
80	0·865	55	0·926	30	0·966	5	0·993
79	0·868	54	0·928	29	0·967	4	0·994
78	0·871	53	0·930	28	0·968	3	0·996
77	0·874	52	0·932	27	0·969	2	0·997
76	0·876	51	0·934	26	0·970	1	0·999

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1. *Regular System.—a. Homohedral. Fig.* 1—12.

b. Hemihedral.—α. Tetrahedron. *Fig.* 13—17.—β. Pentagonal Dodecahedron. *Fig.* 18—20.

2. *Square Prismatic* or *Four-membered System.—a. Homohedral. Fig.* 21—39.

21 and 22: Anatase;—23, 29: Zircon;—24, 27, 33: Molybdate of lead;—25, 26: Hydrated ferrocyanide of potassium;—28, 39: Vesuvian;—30: Acid phosphate of potash ($KO, 2HO, PO^5 + 2HO$) or acid arseniate of potash ($KO, 2HO, AsO^5 + 2HO$);—31: Sulphate, seleniate, or chromate of silver and ammonia;—32: Apophyllite;—34: Cyanide of mercury;—35: Nickel-speiss;—36: Sulphate or seleniate of zinc or nickel;—38: Calomel.

b. Hemihedral. Fig. 40.—Parasulphat-ammon.

3. *Two and two-membered* or *Right Prismatic System. Fig.* 41—80.

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INTRODUCTION.

CHEMISTRY is a branch of Natural Science.

Natural Science embraces the whole range of sensible objects, their properties, and the changes to which they are subject, in so far as these changes are not referable to the inward workings of the human mind.

Some branches of Natural Science consider the several classes of bodies in a state of rest according to their situation, magnitude, form, structure and other physical properties: such are Descriptive Astronomy and Geology, Mineralogy, Botany, Zoology, Animal and Vegetable Anatomy. Other branches of Natural Science take into consideration the changes to which the various classes of bodies are subject, without reference to the causes by which these changes are brought about; *e.g.*, Physical Astronomy and Geology, Animal and Vegetable Physiology, Nosology, Therapeutics. Lastly, Physics and Chemistry regard these changes, not according to the classes to which the bodies belong, but according to the several causes by which the changes are produced. All the changes to which the bodies of the universe are subject may be referred to the following causes or *Forces*.

I. *Repulsion:* which manifests itself, either in the form of Impenetrability, or in that of Expansive Force.

II. *Attraction:* which includes

1. *Mechanical Attraction,* by which bodies are drawn together without any alteration of their properties excepting as regards the space which they occupy; and this may be subdivided into—
   a. *Gravitation,* or Attraction acting at a distance and between large masses.
   b. *Cohesion,* or Attraction between bodies of the same kind, and at immeasurably small distances only.
   c. *Adhesion,* or Attraction between bodies of different kinds, acting at immeasurably small distances only, and producing a heterogeneous mass.
   d. *Chemical Attraction, Affinity* or Attraction between bodies of different kinds, acting at immeasurably small distances only, and producing a homogeneous mass.

III. *Vital Force,* or that peculiar power by which the most important alterations in living organized bodies are produced.

All changes produced by mechanical Attraction belong to the province of Physics; the phenomena resulting from vital force to that of Animal and Vegetable Physiology.

Chemistry relates exclusively to those changes of bodies which are brought about by Affinity. Now since these changes consist—(1) in the combination of dissimilar bodies into a homogeneous mass, and (2) in occasionally resulting separations of dissimilar kinds of matter from a homogeneous mass, it follows that Chemistry may be defined as the science which treats of the combination of dissimilar bodies into homogeneous masses, and of the separation of dissimilar bodies from homogeneous masses.

The range of Chemistry thus marked out is enlarged by the following considerations.

1. By a short account of Cohesion and Adhesion.

2. By the enumeration of the physical properties of the elementary bodies and of the compounds formed by their mutual affinities, particularly of those which do not come within the province of Mineralogy.

On the other hand, the range of the science is narrowed by the consideration that the relations of the Imponderables need not be treated in all their detail, inasmuch as the study of these bodies forms an important branch of physical science.

Chemistry, regarded as an independent science embracing the whole range of chemical knowledge and regarding the chemical properties of the various kinds of matter without reference to any application of them beyond the bounds of the science itself, is distinguished by the name of *Pure, Theoretical* or *Philosophical Chemistry*. And inasmuch as particular branches of it serve to throw light on other sciences, these several branches have received the names of *Physical, Mineralogical, Physiological, Medical, Agricultural* Chemistry, &c.

Chemistry is an *Art* as well as a *Science*. For it teaches not only what combinations of dissimilar bodies into homogeneous masses and what decompositions of these latter are possible; but likewise what rules must be followed, what mechanical means must be adopted to bring about these combinations and decompositions. This is *Practical Chemistry*. It is subdivided into *Synthetical Chemistry* the object of which is the union of dissimilar bodies into homogeneous masses; and *Analytical Chemistry* which teaches how to detect the several constituents of a compound body and estimate their quantities. The art of *Assaying* or *Docimasy*, which relates to the detection and estimation of the precious metals in their various compounds, is a branch of analytical chemistry.

Applied Chemistry comprehends the art of preparing the various substances used in the ordinary business of life, in so far as such preparation is based on chemical principles. Its divisions are: *Pharmaceutical Chemistry* which relates to the preparation of substances used in medicine; and *Technical Chemistry* which is concerned with arts and manufactures. This latter is again subdivided according to the several products whose preparation it embraces,—and more particularly into the following branches: viz. *Metallurgy*, or the production of metals: *Lithurgy*, or the chemistry of minerals: *Hyalurgy*, or the chemistry of glass-making: *Phlogurgy*, or the chemistry of combustible bodies: *Halurgy*, or chemistry of salts, acids and alkalis: *Chromurgy*, or chemistry of colours: *Zymotechny*, or chemistry of fermentation, &c.

Historical Survey.

In ancient times the progress of chemistry was slower, in modern times it has been more rapid than that of any other science. Up to the end of the seventeenth century, chemical knowledge was confined to a few isolated facts, either relating to metallurgy and other chemical arts or to the preparation of medicines, or such as were accidentally discovered during the fruitless search of the alchemists after the philosopher's stone, the transmutation of metals, &c. The marshalling of these facts into a regular system was begun by Becher and Stahl about the end of the seventeenth, and brought to a more advanced stage by Lavoisier towards the end of the eighteenth century.

Among the nations of antiquity the Egyptians appear to have possessed the greatest amount of chemical knowledge. They prepared sal-ammoniac, soda, common salt, vitriol, glass, enamel, tiles, painted earthenware, several metals and metallic alloys, soap, beer, vinegar, various medicines and pigments, and knew how to fix colours on silk by means of mordants, and to preserve dead bodies from decay. The knowledge of the Egyptians extended itself to other nations, particularly the Jews and Greeks. Whether the Chinese, who have long been acquainted with the preparation of sulphur, nitre, gunpowder, borax, alum, porcelain, verdigris, paper, together with dyeing and the formation of various metallic alloys, are partly indebted to the Egyptians for their knowledge—is a question which must remain undecided.

The Greeks sought to penetrate the secrets of nature less by accurate observation than by speculative enquiry. The assumption of the four elements (fire, air, earth and water) by Anaximander and other Grecian philosophers affords evidence however of a right comprehension of the four principal states in which matter can exist. Less conformable to nature is the opinion adopted by Aristotle and others that all matter is essentially the same, and that the various forms of it are due merely to differences of shape in the ultimate particles. The Romans derived all their chemistry, as indeed all the rest of their knowledge, from the Greeks without making the smallest extension of it. The migration of the northern nations and the overthrow of the Roman empire put a stop to the progress of science in Europe.

On the other hand, from the seventh to the eleventh century, the sciences, and chemistry in particular, obtained protection and cultivation among the Arabs who had spread themselves over Spain and the north of Africa. Their chemical investigations were chiefly directed to the preparation of medicines and the conversion of base into noble metals. They aimed at preparing substances which, like the philosopher's stone, should free the base metal from its imperfections or blemishes and thereby convert it into a noble metal: they believed also that such a substance or one of like nature would restore the sick to health and even render man immortal. Hence they laid the foundation of Alchemy. Geber, one of the earliest chemists, who lived in the eighth century, was acquainted with milk of sulphur, nitric acid, aqua regia, solution of gold, nitrate of silver, corrosive sublimate, red oxide of mercury, the preparation of litharge, &c. Albukasis, towards the end of the twelfth century, described a form of still like that at present used in the distillation of brandy; also the distillation of vinegar and wine. The words *Alkali*, *Alcohol*, *Aludel*, &c., which are still in constant use, originated with the Arabs.

The crusades served to transplant the chemical knowledge and views of the Arabs into Europe, where, agreeably with the mystical tendencies of the age, the theory of transmutation found especial favour; and while it raised up persevering alchemists who employed themselves in experiments laborious as they were fruitless for the purpose of obtaining gold from the baser metals, at the same time gave birth to a host of impostors who turned the credulity of others to their own account. This rage for alchemy continued in Europe from the thirteenth to the seventeenth century, and though it failed in attaining the end proposed, gave rise to the discovery of a mass of facts which, had it not been for this thirst for gold, would in all probability have long remained unknown. Among the most renowned of the alchemists were: Arnold de Villa Nova in the thirteenth century, Raimund Lully in the fourteenth, Basil Valentine

(the discoverer of several compounds of antimony and also of ammonia) in the fifteenth, Paracelsus (the first public teacher of chemistry, who prepared many powerful medicines, particularly preparations of mercury) in the sixteenth, Van Helmont (who even at this early period propounded many philosophical views and was the first to distinguish various aeriform bodies by the name of *Gases* from common air), and Libavius in the seventeenth.

Independently of the reigning pursuit of alchemy there arose in these times many men who either devoted themselves to philosophical research like Roger Bacon and Albertus Magnus in the thirteenth century; or exposed the delusions and impostures of the alchemists, like Kircher, Conring, Guibert, Gassendi and Kepler; or were the authors of scientific works, like George Agricola (*de re metallica*, 1546), Lazarus Erker (*Aula subterranea*, 1574) and several others.

Towards the end of the seventeenth century, chemistry received an unexpected extension from the researches of Newton on attraction and light and from the experiments of Torricelli, Guericke and Boyle on the vacuum. About the same time, several salts were discovered by Glauber, phosphorus by Brandt and Kunkel, sweet spirits of nitre and several glass-fluxes by the latter, artificial volcanos by Nicholas Lemery (author of the *Cours de Chimie*), and boracic acid and the alum-pyrophorus by Homberg.

At the very beginning of the eighteenth century, George Ernest Stahl, by applying the already published views of Albertus Magnus and Becher (author of the *Physica Subterranea*) respecting that most important of all chemical processes, *Combustion*, to the whole collection of facts discovered by himself and others, and thus uniting them into a connected whole, laid the foundation of the first system of Chemistry. This system received the name of the *Phlogistic Theory*, because Stahl assumed that all combustible bodies contain one and the same principle of combustion, called *Phlogiston;* the escape of this substance from a heated combustible body being supposed to produce the phenomena of combustion, and its addition to a burnt body to restore the combustibility of that body. In this system Phlogiston and the dephlogisticated metals or metallic earths (metallic oxides of the present system) were regarded as elements and displaced the four elements of the Grecian philosophers. From this time forward chemistry received more scientific cultivation, and discoveries accumulated more and more, until towards the end of the eighteenth century a reform of the system became indispensable.

In 1718, Geoffroy published the first *Table of Affinities*. Boerhaave published in 1732 a chemical work containing many original experiments on light, heat, &c. Hales in 1724 instituted several experiments on the air and other aeriform bodies. These experiments were however much more successful in the hands of Black, who in 1756 showed that the kind of air given out by fermenting liquids and evolved from chalk by the action of acids is different from atmospheric air; and thus directed the attention of experimenters to the more accurate investigation of aeriform bodies. Margraff, 1754—1759, first established the existence of magnesia and alumina as distinct earths, the only earths previously recognised being lime and silica; he also produced sugar from native plants, and discovered the phosphates in urine. Scheele, between the years 1773 and 1786, discovered, with very slender means, chlorine, the hydrofluoric, nitrous, prussic, tungstic, molybdic, arsenic, tartaric, citric, malic, lactic, gallic, and uric acids; also baryta, manganese

(partly), oxygen gas (discovered just before by Priestley); he also demonstrated the presence of phosphoric acid in bones, and instituted many ingenious experiments on light and heat, which led him to the adoption of a new theory of combustion. Bergman perfected the doctrine of Affinity and made several experiments on carbonic acid and other matters, besides many successful analyses of mineral substances. Cavendish, who first collected gases over water instead of receiving them in bladders, was also the first to distinguish hydrogen; he likewise discovered the formation of carbonic acid by the combustion of charcoal, the composition of water and of nitric acid (1765—1785). Priestley, who first collected gases over mercury, discovered in 1770 and the following years, oxygen gas, protoxide of nitrogen, carbonic oxide, ammoniacal, sulphurous acid and muriatic acid gases and the gaseous fluoride of silicon: he also first observed the disengagement of oxygen gas from the green parts of plants.

Antoine Laurent Lavoisier, whose philosophical career, begun in 1770, was ruthlessly cut short in 1794 by the guillotine of Robespierre, not only perceived the defects which later discoveries had made manifest in Stahl's theory, but availed himself of these discoveries together with certain experiments of his own, made with a degree of accuracy in the determination of weights and volumes quite unknown before his time, in order to establish a theory in opposition to the phlogistic, and thence called the *Antiphlogistic* theory:—attempts at the establishment of such a theory had been made by Rey in 1630 and by Mayow in 1670, but without success.

The long established fact that combustible bodies, such as metals, do not lose but gain weight when burnt (an attempt at explanation had been made by supposing a fixation of the fiery particles to take place) was placed in a clearer light by Lavoisier, who showed that this increase of weight is exactly equal to the weight of the oxygen gas absorbed by the combustible body in the act of burning. On the other hand, he showed that in the conversion of a burnt body into a combustible body, a decrease of weight takes place in spite of the phlogiston which was supposed to be absorbed. He denied the existence of phlogiston, regarded combustion as the combination of a combustible body with oxygen, accompanied by a development of light and heat, and the conversion of a burnt into a combustible body as resulting from the separation of oxygen. To him also we are indebted for the discovery that the diamond is carbon, that carbonic acid is a compound of carbon and oxygen, that water is decomposed by red-hot iron, that the earthy matter deposited when water is heated in glass vessels is derived from the glass itself—as well as many well devised investigations on heat, respiration, transpiration. &c.

From this time forward Chemistry advanced with twofold rapidity, partly through the zeal of the adherents of the new theory, partly through that of their opponents, who, while they endeavoured to overthrow it by new researches, really contributed to its establishment and extension. Berthollet who in 1787 was the first to attack the new theory acquired great reputation by his researches upon Chlorine and upon the doctrine of affinity. Fourcroy undertook, particularly in connexion with Vauquelin, more exact analyses of organic substances and several other investigations. The latter in the course of his numerous analytical researches discovered chromium, glucina, and several vegetable substances. Klaproth, to whom mineral analysis is most deeply indebted,

discovered zirconia, titanium, uranium and tellurium. Richter in his *Stoichiometry*, laid the foundation of the doctrine of definite and simple proportions by weight according to which bodies combine. Prout investigated with great accuracy the chemical relations of several metals, and successfully combated Berthollet's doctrine of affinity. Smithson Tennant was the first who separated carbon from carbonic acid: he also discovered osmium and iridium. Wollaston discovered palladium and rhodium in platinum ore.

The discovery of Galvanic electricity by Galvani, to which Volta (the inventor of one of the most useful forms of the Eudiometer) gave increased power by means of his *Pile*, furnished the chemist with a new means of decomposition, which not only served to confirm Lavoisier's theory of the compound nature of water, but also, in the hands of the highly-gifted Sir Humphrey Davy, to resolve the hitherto undecomposed alkalis and earths into peculiar metals and oxygen. Besides this, Davy enriched the science by his investigations on galvanic electricity, flame, and the compounds of chlorine. At the same time also, Gay-Lussac and Thénard investigated the nature of the chlorine compounds and of the metals which form the bases of the alkalis, and were the first to effect the complete separation of fixed organic substances into their elements. Gay-Lussac also extended the science of Heat, particularly as relates to evaporation, established the *Law of Volumes*, which governs the combination of elastic fluids, and made a most accurate investigation of the chemical relations of iodine, the discovery of which had just before been made by M. Courtois.

The highest degree of exactness in the investigation of the proportions by weight in which bodies combine was attained by Berzelius, whose researches in this department of the science led him to adopt and confirm the almost forgotten views of Richter. By a vast number of experiments he ascertained the proportions by weight in which all the elementary bodies combine one with another. By improvements in Klaproth's methods of mineral analysis, he succeeded in decomposing several new minerals, and thereby established the existence of cerium, selenium, thorium, and partly also of lithium, as new elements. At the same time also, but with less reference to direct experiment, Dalton developed Richter's doctrine in the form of the new atomic theory: he likewise made some most able investigations upon heat, particularly on the formation of vapour.

Within the last few years, the electro-chemical phenomena have been most successfully investigated by Faraday, De Larive, Becquerel, and others; and the field of organic chemistry has, by the labours of Berzelius, Liebig, Wöhler, Mitscherlich (the founder of the theory of *Isomorphism*), H. Rose, Mulder, Chevreul, Dumas, Pelouze, Laurent, Malaguti, and many others,—been enlarged to such an extent, that it has become almost a new science.

Cohesion.

Cohesive Power. Attraction of Aggregation. Cohäsionskraft. Zusammenhäufende Verwandtschaft. Cohæsio. Attractio aggregationis, Cohésion.

The attraction which bodies of the same nature exhibit towards each other when brought into immediate contact. The consequence of this action is the combination of a number of homogeneous bodies into a whole of the same nature. The product so formed is called an Aggregate.

The combination may be destroyed by a mechanical pressure or thrust strong enough to overcome the cohesion.

The force of cohesion varies with the temperature and with the nature of the body.

It is a general rule that the cohesion of a body diminishes as its temperature increases. A heated liquid forms smaller drops than a cold one (sulphur alone forms an exception to this rule, increasing in consistence as its temperature rises); hard bodies when heated generally become softer, sometimes even fluid, provided no chemical changes take place in them.

Bodies may be divided according to their cohesive power into four classes. (1.) *Imponderable Bodies*, as light, heat, electricity and magnetism. In these the repulsive force the antagonist of the attractive predominates, and none of the phenomena which they exhibit are such as to make it probable that a mutual attraction or cohesion is exerted between their particles. (2.) *Ponderable Elastic Fluids*, viz. Gases and Vapours. In these, the ponderable matter is rendered so highly elastic by its combination with heat that, generally speaking, all their known properties may be explained without supposing them to be possessed of cohesion, unless perhaps Faraday's experiments (*Qu. J. of Sc.* 3, 354, also *Ann. Chim. Phys.* v. 298) on the different velocities with which different gases flow through narrow tubes may be explained by supposing different degrees of cohesion to exist in the various gases. (3.) *Liquids.* These may be regarded as combinations of ponderable matter with smaller quantities of heat, sufficient to produce a remarkable diminution of the cohesion peculiar to solids, but not to occasion any sensible repulsive power. (4.) *Solids.* In these the cohesive power exhibits itself in its highest degree.

Cohesion of Liquids.

This force shows itself in the tendency towards the spherical form, inasmuch as the effort of all the several particles of a liquid mass to approach each other as closely as possible must result in the assumption of the spherical form. Since, however, the liquid mass is subject to the influence of other forces, gravitation and adhesion for instance, the spherical form can never be perfect: *e. g.*, mercury upon glass, water upon glass which has been smeared with fat or lycopodium.

The cohesion of liquids is also shown by a certain resistance which they offer to the force of gravitation, when, in order to obey that force, they would be obliged to divide themselves into very small parts,—supposing that the cohesion is not at the same time opposed by adhesion or agitation. Thus mercury will not run through fine muslin, nor water through a metal sieve covered with fat or lycopodium.

The cohesion between the particles of a liquid being small and equal in all directions, the slightest force is sufficient to disturb them. The motion of one part does not produce an equal and parallel motion in all the rest of the mass, whereas in solid bodies the application of a slight force produces, not a disruption of the parts, but an equal and similar motion in the whole mass.

Different liquids exhibit different degrees of cohesion: the cohesive power is for the most part very nearly proportional to the density.

Cohesion of Solids.

This force shows itself particularly in three ways.

1. In an individual portion of a solid body.

In this case cohesion shows itself by the resistance which, up to a certain limit, it opposes to any mechanical force tending to separate the particles. Hence the force which is exactly sufficient to overcome the cohesion of a body affords a measure of that cohesion. (On the tenacity of metals, *vid.* Morveau, *Ann. Chim.* 71, 194; also *Gilb.* 34, 209.)

2. When separate masses of like nature come into close contact with one another.

If the surfaces are uneven, the points of contact are infinitely small, and the cohesive force imperceptible. But if the bodies touch each other by large flat surfaces, *e. g.*, well polished glass or metal plates, the number of points of contact is greatly increased, and the cohesion becomes very evident. If the surfaces touched at all points, the cohesion of the bodies would be as powerful in this direction as in any other.

3. When bodies pass gradually from the liquid to the solid state.

In this case the particles unite.

(1.) In masses of indefinite external form, which refract light singly in every direction, are equally easy or equally difficult to separate in all directions, and when broken exhibit a conchoidal fracture; *Amorphous bodies*, such as glass and gum.

Or,

(2.) In masses of geometrical shape, bounded by flat surfaces, and having solid and dihedral angles of constant magnitude for the same matter and form,—having as great a degree of transparency as is consistent with the nature of the matter of which they are formed,—for the most part, refracting light doubly in certain directions—and finally, presenting greater facilities of separation or cleavage in certain directions lying in determinate planes than in others; *Crystals.*

Many bodies are more disposed to the amorphous, others to the crystalline form: a great many may however be obtained in one state or the other, according to circumstances.

Crystallization.

To enable a body to crystallize, it must first be brought into the liquid or gaseous state. This is effected either by elevation of temperature, in consequence of which the body melts (Copper, Bismuth) or sublimes (Sal-ammoniac, Iodine),—or else by causing the body to combine with another ponderable body, which either at the ordinary or at a somewhat higher temperature is liquid or gaseous (salts dissolved in water, sulphur in sulphuret of carbon, sulphate of baryta in oil of vitriol, camphor, benzoic acid, &c. in alcohol, iodine in hydriodic acid gas):—the causes which have brought the body into the fluid state must subsequently be removed.

1. If heat has been the only liquefying power, or if it has served to render a solid more soluble in a fluid, cooling must be resorted to. To obtain definite crystals from a melted mass (sulphur or a metal for instance), it is allowed to cool to a certain extent only, and the yet remaining liquid portion, which if left in contact with the first formed crystals would unite with them into an amorphous mass, poured out. The vapour of sulphur, iodine or sal-ammoniac is conducted into a colder part of the apparatus, where it deposits crystals. A warm solution of various salts in water, of sulphur in sulphuret of carbon, of camphor, &c.

in alcohol deposits, upon cooling, in the crystalline state that portion of the solid body which the liquid is not capable of retaining in solution at the lower temperature.

A remarkable anomaly is often observed in the cooling of such solutions, viz., that when kept perfectly still and in covered or stoppered vessels, they may, without losing their liquid form, be cooled much below the temperature at which they usually crystallize; under these circumstances, a sudden crystallization may be brought about by agitation, the introduction of a solid body, &c., &c. Of this the following are examples. Water, when cooled in open vessels and not at absolute rest, below 0° C., solidifies in a crystalline mass: but in stoppered bottles or thermometer bulbs, it may often be cooled as low as — 6° without freezing, and when the vessel is shaken or opened, or a piece of ice put in, crystallization suddenly takes place, the crystals beginning to form at several points at once and quickly radiating through the liquid; the temperature at the same time rises to 0°. The formation of mists over the surface of lakes sometimes observed at the moment of freezing is perhaps dependent upon this action. Pure phosphorus melted in a capsule under warm water will remain all night in the liquid state at a temperature of 4·5° C., and solidify when poured out upon the hand. (Clark, *Ed. Journ. of Sc.* 7, 281.) Phosphorus boiled with caustic potash retains its fluid state at the ordinary temperature for months, when kept under the solution, and solidifies when touched with a dry solid body. (Poggendorff.) Sulphur sublimed in small melted drops retains its fluid state over night at the ordinary temperature, and solidifies when touched with any solid body. (Faraday, *Qu. Jour. of Sc.* 21, 392; also *Pogg.* 7, 240.) Sulphur precipitated by water from chloride of sulphur remains fluid at the bottom of the liquid, but solidifies immediately on exposure to the air. (Poggendorff, *Pogg.* 7, 241.) Glacial acetic acid, which in open vessels crystallizes at + 16° C., may be cooled to — 12° even with agitation in stoppered bottles without solidifying: if, however, the vessel be opened and shaken, it crystallises at + 15°, even when the outward air is warmer than the acid, the crystallisation beginning at the top and quickly shooting through the whole mass. (Löwitz, *Crell. Ann.* 1790, 1, 209; Geiger, *Schw.* 15, 231.) Oil of anise, when cooled at rest in a closed vessel, often remains liquid till it is shaken, crystallization then taking place instantaneously. (Buchner, *Repert.* 15, 64.) Scheererite after fusion may be kept in the liquid state at ordinary temperatures for several days, and crystallizes instantly on being touched with a platinum wire or glass rod. (Stromeyer, *Kastn. Archiv.* 10, 114.)

Many salts dissolved in hot water exhibit this anomaly, especially sulphate of soda. A hot solution consisting of equal parts of water and crystallized Glauber's salt (sulphate of soda with 10 atoms of water of crystallization) does not crystallize either on slow cooling, or when quickly cooled by immersion in cold water,—whether it be contained in a barometer-tube freed from air by boiling; or in an exhausted well closed vessel; or in an open vessel with a layer of oil of turpentine upon its surface, (Gay-Lussac); or in a vessel containing air, either well stopped or merely furnished with a loose cover, (Schweigger); or in an open vessel under a bell jar full of air and closed at the bottom with a water-joint; or in open bottles placed in a quiet situation; or in an open glass enclosed in a stoppered vessel containing air and some potash to dry it, in which Glauber's salt effloresces and when washed down again does not cause instant crystallization but dissolves. (Ziz.) The crystallization of

a solution cooled in this manner is often brought about instantaneously, often again after a short time: (1.) By agitation, viz., when the solution has been cooled in an open vessel. (2.) By access of air caused by opening the vessel, the crystallization taking place the more quickly in proportion to the size of the opening; some degree of motion appears also to be necessary. In this case, the crystallization begins at the top where the solution, the vessel, and the air come in contact with each other; it is only when a particle of dust falls in on opening the vessel that the crystallization begins a little under the surface. When the solution has been cooled in vacuo, a bubble of air, hydrogen, carbonic acid, or nitrous gas is sufficient to set up the crystallization. (Gay-Lussac.) (3.) By contact of the solution with a solid body (a glass rod, flint, iron wire, crystal of Glauber's salt, or a grain of dust floating in the air.) These bodies do not bring about the crystallization when they have cooled in contact with the hot solution, nor (excepting Glauber's salt) when they are wetted or warmed before contact with the solution. (Ziz.) In these cases crystallization is effected by the action of foreign bodies. If a solution of 8 parts of Glauber's salt in 9 parts of water be left to crystallize, the whole then warmed in a flask to between 50° and 55° C., till only about $\frac{1}{3\,2}$ of the crystals remain undissolved, and the flask corked up and cooled, it often happens that the remaining crystals, instead of causing the rest to crystallize, are themselves completely dissolved,—slowly when the flask is inclined in such a manner as to bring them in contact with the upper strata of the liquid, more quickly on agitation, which however is very likely to cause crystallization. If, on the other hand, the solution formed between 50° and 55° be poured off from the crystals into a basin and allowed to crystallize, the mother-liquid thus obtained will not dissolve the $\frac{1}{3\,2}$ of the crystals above mentioned. There are therefore two solutions to be distinguished, (1.) The *saturated* solution, *i. e.*, the liquid which remains after crystallization of the superabundant quantity of salt, from a hot solution in an open vessel, and, (2.) The *supersaturated* solution, *i. e.*, the solution saturated at a high temperature and cooled in a close vessel; this latter can even dissolve an additional quantity of salt but deposits at a lower temperature crystals of sulphate of soda containing 1 atom of the salt and 8 atoms of water. (H. Ogden.) A solution of 2 parts of Glauber's salt in 1 part of hot water yields on cooling in close vessels hard transparent crystals of sulphate of soda with 8 atoms of water, which, when the supernatant liquid is made to crystallize by any of the preceding methods immediately become opaque. (Coxe, Ziz.) When 51 parts of crystallized Glauber's salt are dissolved in 49 of water, and the solution after cooling below 10° C. made to crystallize suddenly by any of the preceding methods, nearly $\frac{2}{3}$ of the Glauber's salt is deposited, and the temperature rises to 13° C. This is attributed by Thomson to the conversion of liquid water into solid water of crystallization, a supposition agreeing pretty well with calculation (the development of heat consequent on the passage of the salt from the liquid to the solid state must however be included in the calculation. Gm.) The assertion of Thénard (*Schw.* 15, 257), that after this crystallization there remains a mother-liquid which is no longer saturated with salt at the existing temperature seems to be erroneous. Thomson, on the contrary, finds that the mother-liquor, from its rise of temperature, holds in solution a corresponding quantity of salt, a great part of which crystallizes out when the temperature is brought back to 10°.

A hot concentrated solution of chloride of calcium cooled in a stop-

pered bottle crystallizes when agitated, without requiring the bottle to be opened, the temperature at the same time rising very considerably. (Coxe.) The addition of a few drops of oil of vitriol or oxalate of ammonia does not cause it to crystallize; but crystallization takes place when cold water is poured upon the liquid or a stream of dry air directed upon it. (Ogden.) A solution of 1 part of crystallized carbonate of soda in 4 parts of warm water, when cooled below + 10° C. crystallizes on opening and shaking the bottle; the temperature rising about 8°. A highly concentrated solution of acetate of soda remains liquid when cooled to + 10° in a loosely stopped vessel: but on pouring it into another vessel it solidifies to a fibrous mass, the temperature rising to 52·5°. (Gm.) Under similar circumstances Hashoff (*Br. Archiv.* 38, 326) obtained, upon stirring, a rise of temperature of 59° C. The introduction of a crystal of acetate of soda produces crystallization, but not so quickly as in the case of sulphate of soda. (Ogden.) A hot solution of sulphate of magnesia often remains fluid when cooled in close vessels, and yields granular crystals when shaken. (Coxe.) A drop of alcohol produces in the solution a nucleus from which the crystallization radiates. (Ogden.) A mixture of nitre and sulphuric acid yielded, after heating for some time, a clear liquid which did not crystallize on cooling till a crystal of nitre was thrown in, a rise of temperature then taking place. (Green, *Gilb.* 70, 320.) The following salts exhibit similar phenomena to the above:—Hyposulphate of soda, (Heeren); carbonate, phosphate and borate of soda, (Gay-Lussac); nitrate of lime, sulphate of magnesia, sulphate of copper and nitrate of silver, acetate of lead, (Fischer, *Schw.* 12, 187); nitrate of ammonia, bisulphate of potash, bichromate of potash, chloride of barium, sulphate of magnesia and ammonia, sulphate of zinc, ferrocyanide of potassium, oxalate of ammonia, tartrate of potash and soda, and tartrate of antimony and potash. (Ogden.) Warm solutions of alum, protosulphate of iron and sulphate of copper deposit considerable quantities of crystals upon cooling; but opening of the vessel and shaking bring out a fresh quantity. (Coxe.) Nitro-saccharic acid also exhibits this property. (Mulder, *J. pr. Ch.* 16, 293.) The following salts, on the contrary, crystallize out from a warm solution on the slightest lowering of temperature:—Sulphate and hydrochlorate of ammonia; sulphate, chlorate, nitrate and neutral chromate of potash; chloride of potassium, chloride of sodium; baryta, strontia, nitrate of baryta, sulphate of magnesia and potash, nitrate of lead, corrosive sublimate and oxalic acid. (Gay-Lussac, Ogden.) Generally speaking, those salts which exhibit the anomaly crystallize in combination with a large quantity of water of crystallization (bichromate of potash and nitrate of silver excepted), and those which do not exhibit it, with little or no water of crystallization. This anomaly is explained by Berthollet (*Statique Chim.* 1, 32,) and by Gay-Lussac, on the supposition of a sluggishness of the ultimate particles of the salt. So also Thénard supposes that the particles are brought by agitation into different relative positions. (It must be observed however that shaking in closed vessels often fails to produce crystallization.) At all events it may be admitted that in those cases in which the cohesive force has gained the preponderance over other forces, such as the affinity of a body for heat or for ponderable solvents, mechanical disturbance is often required to bring it into active operation. *Compare* Gay-Lussac (*Ann. Chim.* 87, 225, also Schw. 9, 70; likewise *Ann. Chim. Phys.* 11, 301); Schweigger (*Schw.* 9, 79), Ziz. (*Schw.* 15, 160), Thomson (*Ann. Phil.* 10, 169); H. Ogden (*N. Ed. Phil. J.* 13, 309).

II. If the crystallizable body has been liquefied by combination with another ponderable body, the latter must be separated from it. This is effected either by driving off the latter in the form of vapour, at a high or a low temperature, in the open air or in vacuo, as the case may be; or else by removing the solvent by virtue of its affinity for another ponderable body. Thus nitre crystallizes from an aqueous solution on the addition of alcohol, camphor from an alcoholic solution on the addition of water, iodine from its solution in hydriodic acid gas on the introduction of a small quantity of chlorine.

During crystallization the following phenomena are observable:—1. The more slowly the liquefied body is brought back to the solid state, and the more the liquid is kept at rest, the smaller is the number and the greater the size and regularity of the crystals; but if the solvent be cooled or separated quickly, the crystals are numerous but small and ill defined. For in the former case, the particles of the solidifying body have time to unite themselves regularly with those which separate first from the fluid and form nuclei of crystallization; if on the contrary the crystallization takes place rapidly, a great number of particles solidify at the same time, each forming a nucleus to which other portions may attach themselves, and thus we obtain a number of crystals irregularly formed and interlacing each other in all directions. In this consists the difference between sugar-candy and loaf-sugar; similarly, all granular and fibrous bodies, such as statuary marble and fibrous gypsum, must be regarded as collections of imperfectly formed crystals equal in number to that of the grains or fibres. To obtain crystals as large and regular as possible, Leblanc recommends (*J. Phys.* 55, 300) to allow a solution not quite saturated to cool slowly, so that none but distinct crystals may be formed, then to pick out the best formed of these and lay them separate from one another in a solution of the same salt, which by gentle warming in contact with the salt has been made to hold in solution a quantity of it just a little greater than that which it can retain at the ordinary temperature, so that it may deposit this excess on the crystals laid in it. This treatment is repeated till the crystals have obtained the desired magnitude, care being taken to turn them frequently, because the surfaces resting on the bottom are in a less favourable position than the rest for taking up fresh particles. The trouble of repeatedly preparing a slightly supersaturated solution may be saved by suspending in the upper part of the liquid a quantity of the salt contained in a bag of muslin or a funnel. For whenever the temperature rises, the warmer part of the liquid will come to the surface, where it will dissolve a portion of the suspended salt, and then becoming specifically heavier, it will sink to the bottom of the vessel where the crystals are placed: thus the crystals will continue to grow, and nothing further will be necessary than to turn them frequently.

2. Generally speaking, crystals exhibit, so far as can be observed, the same external form on their first formation, that they have at a subsequent stage. Probably the primitive form is first developed and passes into the secondary by the subsequent annexation of matter according to fixed laws. Thus the octohedron of alum exhibits, as lately observed by F. Richter (*Zeitschr. Ph. v. W.* 3, 348), the same truncations of the edges and summits at its first formation as after its complete development. When however the formation of crystals is suffered to go on at intervals and in liquids of different nature, the external form may be greatly modified. This may be observed in certain crystallized minerals which often possess a nucleus and an envelop of different colours. Fluor-spar exhi-

bits, according to F. Richter (*Zeitschr. Ph. v. W.* 2, 111), the following forms: a rose-coloured octohedron within a green cube; a yellow cubo-octohedron (*fig.* 4) whose octohedral faces alone are covered with a violet layer; a blue dodecahedron (*fig.* 3) enveloped in a green cube; a cubo-octohedron (*fig.* 4) within a pyramidal cube (*fig.* 9), &c. In such cases the inner and outer mass always exhibit parallel cleavage. Similar phenomena are also seen according to Richter in calcspar and other minerals.

3. Crystals are formed in situations where the principle of fluidity is removed from them, or where they are led to attach themselves by adhesion. Hence they form on the surface of the liquid in so far as evaporation and cooling by the influence of the air, or adhesion of the air to the crystals can give rise to their production; also on the bottoms and sides of the containing vessels, inasmuch as these abstract heat, and exert adhesive power on the crystals; lastly, on solid bodies immersed in the liquid, such bodies acting by adhesion. For the most part, crystals deposit themselves more easily on wood and string than on porcelain, glass, and metal; more easily on porcelain than on glass; on rough than on smooth glass:—compare Griffiths (*Ann. Pharm.* 22, 210). Hence it is easy to explain the fact that when a glass containing a crystallizable liquid is scratched with a glass rod, the crystals deposit themselves in preference on the scratches. The first-formed mass of crystals serves for the rest to attach themselves to, and attracts them more strongly than foreign bodies would. Thus, according to Löwitz, the introduction of a crystal of nitre into a solution of nitre and Glauber's salt, prepared hot and subsequently cooled, causes the nitre to separate alone: a crystal of Glauber's salt removes only the Glauber's salt; whereas if the solution be left to itself, both salts crystallize out together, the crystals interlacing each other. If a drop of a solution of gypsum be left to evaporate on a freshly cleft surface of a crystal of gypsum, the microscope will show an innumerable collection of crystals of gypsum formed on the surface, all parallel to one another and to the original crystal. If the evaporation takes place on the surface of a foreign body this parallelism is not observed (Frankenheim, *Pogg.* 27, 516.) When a solution evaporates below its boiling-point, the first crystals are usually deposited on the sides of the vessel at the uppermost surface of the liquid: another portion of the liquid often rises through these and yields by evaporation new crystals which ultimately make their way over the edge of the vessel. This is *Efflorescence*. When crystals form at the bottom of a liquid, a current is produced, because the individual crystals take from that part of the solution with which they are immediately in contact as much of the salt as is possible under the existing circumstances; consequently this part of the liquid becomes lighter and rises to the surface, its place being supplied by a more saturated portion of the liquid.

4. When a body crystallizes from solution in a liquid, and the latter is not completely removed by evaporation, there remains a portion called the *Mother-liquor* (*Eau mère, Mutterlauge*). This liquid holds in solution as much of the crystallizing body as is consistent with its quantity and temperature. It often happens, especially when crystallization proceeds rapidly, and the crystalline laminæ in the act of uniting, leave small spaces between them, that small and (even with regard to the same substance) very variable quantities of the mother-liquid remain enclosed in the crystalline mass, forming the *Water of Decrepitation* (*Zerknisterungswasser*). Crystals which contain liquids thus enclosed and do not melt below the boiling point of the mother-liquid, exhibit, when heated, the

phenomena of *Decrepitation* (*Zerknistern*), the vapour given off from the mother-liquid bursting the crystalline mass with violence. This water of decrepitation which, as an accidental mechanical admixture has no influence on the form of the crystal, is altogether different and must be carefully distinguished from the chemically-combined water which certain crystals contain in definite proportion, and which is essential to their crystalline form. Common salt crystallized by slow evaporation from an aqueous solution does not decrepitate; but when crystallized by rapid boiling of the liquid it decrepitates violently. Many forms of calcspar decrepitate, others not. According to Baudrimont (*J. Pharm.* 22, 337), who regards decrepitation as the result of unequal heating of laminar masses (?), the salts which exhibit this property most strikingly are: iodide, bromide and chloride of potassium, bromide and chloride of sodium, sulphate, chromate and bichromate of potash, nitrate of baryta, red ferrocyanide of potassium and cyanide of mercury.

Decrepitation takes place for the most part in those crystals obtained from aqueous solutions, which do not contain chemically combined water: some salts, however, which contain small quantities of combined water, such as bicarbonate of potash, bitartrate of potash, tartar-emetic, and neutral acetate of copper, decrepitate slightly from containing mother-liquid mechanically inclosed in them. The occurrence of decrepitation in chloride of sodium artificially crystallized from an aqueous solution, and its non-occurrence in rock-salt, leads to the supposition that the latter has been crystallized from a state of igneous fusion. There is but one variety of rock-salt that decrepitates when heated, viz., the decrepitating salt of Wielitzka, the decrepitation proceeding however not from mechanically included water, but from hydrogen and other inflammable gases existing in the salt in a high state of condensation. A similar phenomenon is observed in many crystallized minerals occurring in metallic veins, such as heavy spar, calcspar, fluor spar, ironspar, lead spar, galena, iron pyrites, copper pyrites, grey copper ore, &c., which sometimes decrepitate, sometimes not; and in the former case give out, not water, but probably a gas which was enclosed between their laminæ in a highly compressed, perhaps even in the liquid state. (H. Rose, *Pogg.* 48, 354.)

If a solution, in addition to the crystallizing substance, likewise contains others which are less easily crystallizable, the latter will remain in the mother-liquid after the separation of the greater part of the former. This circumstance furnishes a method of purifying easily crystallizable substances by repeated solution, crystallization, pouring off of the mother-liquid, washing with small quantities of the cold solvent, and pressing between blotting-paper. In this method of purification, the formation of large crystals by slow cooling or evaporation is usually preferred, because they present fewer surfaces, and are therefore more easily freed by washing from the adhering mother-liquid. On the contrary, in the new French method of purifying saltpetre, the smallest possible crystals are formed by constant stirring and rapid cooling of the hot solution, because large crystals of this salt contain a larger quantity of mechanically included mother-liquid which cannot be removed by washing. If however it be remembered that the more slowly crystallization takes place, the less is the quantity of mother-liquid inclosed, and moreover that small crystals are much more difficult to free from liquid adhering to their surfaces than large ones, we shall probably agree with Clement and Désormes (*Ann. Chim.* 92, 248), notwithstanding the objections of Long-

champ (*Ann. Chim. Phys.* 9, 200) in giving the preference to slow crystallization. The methodical purification of a salt, saltpetre for example, by crystallization, may be conducted as follows. (1.) The saltpetre is heated with water in a vessel A, till it is dissolved. It is then left to crystallize by cooling, the mother-liquid poured off as completely as possible into another vessel B, by gradually inclining the vessel A; the crystals are then repeatedly washed with a small quantity of cold water, which after such washing is run off as completely as possible into B. (2.) The vessel A is heated with water till the salt is dissolved, and B till $\frac{2}{3}$ of the contained liquid is evaporated; the mother-liquid from B, after the crystals are deposited, is poured into a third vessel C; the crystals in B repeatedly washed as aforesaid; then the mother-liquid and likewise the wash-water from A poured upon the crystals in B. (3.) All three vessels are heated till the crystals in A are dissolved in fresh water, those in B in the mother-liquid and wash-water from A, and the liquid in C sufficiently concentrated. In this manner the process is continued, smaller and smaller vessels being used in the successive stages till the saltpetre in A appears perfectly pure, then that in B, and so on. Nearly all the impurities of the saltpetre collect in the last vessel A; those near it contain small quantities of the salt in an impure state.

5. The formation of crystals is always accompanied by development of heat: this is particularly evident when the crystallization is rapid, and is therefore most conspicuous in the before-mentioned anomalous cases of the sudden crystallization of a cooled liquid. In a few instances crystallization is attended with production of light. (*vide* Light.)

External Form of Crystals.

The number of crystalline forms amounts to several thousands. According to the proportions of their linear dimensions, or *axes*, they may be arranged in a small number of groups, which in Weiss's *System of Crystallography* (*Abh. d. physik. Classe der K. Academie d. Wiss. zu Berlin*, 1814, 1815, S 298), are as follows:—

A. The proportion of the parts may be determined by three linear dimensions or axes, at right angles to each other.

a. The three dimensions equal. *Regular, Spheroidal, Tessular system.* (Reguläres, sphäroëdrisches, tessularisches krystallsystem.)

α. All the faces of the crystal similar; at each end of the axis the relation between the faces in four directions is the same. *Homospheroidal system* (Homosphäroëdrisches system) to which belong the *cube, regular octohedron, rhomboidal dodecahedron, trapezohedron, pyramidal cube, pyramidal octohedron, pyramidal dodecahedron,* &c. (Diamond, sal-ammoniac, common salt, sulphuret of zinc, most simple metals, &c. *Fig.* 1—12.)

β. One half of the similar faces is obliterated by the other half: at each end of the axes a similar relation of the faces exists in two opposite directions only. *Hemispheroidal system* (Hemisphäroëdrisches system). To this belongs, on the one hand, the *regular tetrahedron* formed by the obliteration of four faces of the regular octohedron, with its modifications (Fahlerz, boracite, *fig.* 13—17): and, on the other hand, the *pentagonal dodecahedron* and its modifications, formed by the obliteration of 12 faces of a pyramidal cube. (Iron pyrites, *fig.* 18—20.)

b. Only two axes equal, *Four-membered, Two and one-axis,* or *Square prismatic System* (Viergliedriges, zwei-und einaxiges *oder* quadratisches system), to which belong the *acute* and *obtuse octohedron with a square*

base, the square prism, and the *regular octagonal prism* (Molybdate of lead, zircon, calomel, ferrocyanide of potassium, tin-stone, &c. *Fig.* 21—40.)

c. All three axes unequal.

α. All the similar faces exist: the primitive form to which the others may be immediately reduced is an octohedron with a rhombic base. *Two and two-membered, One and one-axis*, or *Right prismatic system* (Zwei und zwei-gliedriges *oder* ein und ein-axiges system). This comprises the rhombic octohedron (*fig.* 41), the *rectangular octohedron* (*fig.* 47), two double tetrahedrons (one represented in *fig.* 54), the *upright rhombic prism* (*fig.* 44), the *rectangular prism*, and numerous more complicated forms. (Sulphur, nitrate of potash, sulphate of lead, heavy spar, sulphate of magnesia, &c. *Fig.* 41—80.)

β. Part of the similar faces obliterated; the lower fore and upper back *y*-surfaces of *fig.* 54. The primitive form is a rhombic prism with oblique terminal faces, so placed that one diagonal of the terminal faces is perpendicular to two of the lateral edges, the other diagonal inclined to the remaining edges; sometimes the base is obliquely inclined to the obtuse lateral edges (*fig.* 81), sometimes to the acute ones (*fig.* 91). To this system also belongs the *oblique rectangular prism* (*fig.* 82 and 92). *Two and one-membered* or *Oblique prismatic system* (Zwei und eingliedriges system). (Augite, borax, gypsum, phosphate of ammonia, green vitriol, &c., *fig.* 81—119.) A modification of this system is the *one and two-membered* (ein-und zweigliedriges system).

γ. We must here introduce the system discovered by Mitscherlich (*Pogg.* 8, 427) in hyposulphite of lime and protonitrate of mercury, the primitive form of which is a rhombic prism, in which the faces *u* and *ú* have the same value, but the base is obliquely inclined to all the lateral edges: as happens, for example, when the face *α* (*fig.* 99) obliterates the faces *i* and *í*, (*fig.* 120.)

δ. By obliteration of two parallel *y*-faces, and two parallel *ú*-faces (*fig.* 54) at once, and replacing of the latter by two new faces *v*, there arises a rhomboidal prism whose terminal faces are obliquely inclined in such a manner that both their diagonals make oblique angles with the lateral edges of the prism. Only the parallel faces and the diagonally opposed edges and summits are equal and similar. *One and one-membered* or *Doubly oblique prismatic system* (Ein-und eingliedriges system). Sulphate of copper, boracic acid, gallic acid, &c. *Fig.* 121—130.

B. The relation between the parts of the crystal may be determined by assuming 4 linear dimensions, 3 of which, of equal length, are contained in one plane and inclined to one another at angles of 60°: the fourth is placed at right angles to them. *Three and one-axis* or *Rhombohedral system* (*Drei-und einaxiges system*).

a. All the similar faces exist: at each end of the lateral axes, the same relation of the faces exhibits itself both above and below. *Six-membered system* (Sechs-gliedriges system) including the *double six-sided pyramid*, the *six-sided* and *twelve-sided prism*, &c. (Apatite, &c. *fig.* 131—140.)

b. Of each pair of similar and parallel faces one is wanting; at each end of the lateral axes the upper face or faces differ from the lower both in number and situation. *Three and three-membered system* (*Drei-und dreigliedriges system*). The primitive form of this system is the *rhombohedron*, which we may imagine to be formed from the double six-sided pyramid by the obliteration of half of the faces alternately disposed.

(Calcspar, cinnabar, peroxide of iron, sesquioxide of chromium, &c., *fig.* 141—160*.)

The primitive forms of these systems are moreover subject to innumerable modifications from truncations, formation of edges and angles, divisions and curvatures.

The same kind of matter may crystallize in various forms, which however in most cases belong to one single crystalline system only, are compatible with regard to their angles, and may be deduced from a common primitive form. Thus, calcspar occurs in more than 100 crystalline forms which however all belong to the 3 and 3-membered system, and are derivable from an obtuse rhombohedron (*fig.* 141). If we are acquainted with but one form of a crystalline body we may yet conclude that the body might, under certain circumstances, assume all the other forms belonging to the same system. Why the same substances should assume sometimes one sometimes another form belonging to the same system, is not yet satisfactorily ascertained. According to Beudant (*Ann. Chim. Phys.* 8, 5), temperature, electrical condition, the concentration and volume of the liquid, the form and substance of the containing vessel, the state of the barometer and hygrometer, have no influence on the form assumed. Bouchardat also (*Ann. Chim. Phys.* 52, 296), obtained common salt constantly in cubes, and alum in octohedrons, differing only in magnitude, whether the crystallization took place in vessels of sulphur, graphite, or metals of the most various kinds. The greatest influence appears to be exerted by the presence of foreign bodies in the crystallizing liquid. Sal-ammoniac, which crystallizes in octohedrons from a solution in pure water, produces cubes when the liquid contains a large quantity of urea, and cubo-octohedrons when a small quantity of urea or boracic acid is present. Common salt, which when alone crystallizes in cubes, assumes the octohedral form when the liquid also contains urea, and the cubo-octohedral when boracic acid is present. Chloride of potassium which separates in cubes from a pure aqueous solution, deposits cubes with truncated edges when the liquid also contains corrosive sublimate (*fig.* 5). A solution of alum, to which a little alcohol has been added, yields cubes instead of octohedrons; the addition of hydrochloric acid to the same solution causes the alum to crystallize in cubo-icosahedrons (*fig.* 20); the addition of borax gives rise to cubo-octo-dodecahedrons (*fig.* 8). Protosulphate of iron, which by itself crystallizes in the form shown in *fig.* 111, yields, according to Beudant, when its solution is mixed with sulphate of zinc or sulphate of magnesia, crystals which exhibit only the *i*-, *u*- and *c*- faces; but if hydrochloric acid, borax, or

* Crystallographical Nomenclature of different writers:—

Weiss.		Mohs.	Naumann.	Breithaupt.	Hausmann.
Reguläe		tessularisch	tesseral	tessularisch	isometrisch
4 gliedrig oder 2 u. 1 axig.		pyramidal	tetragonal	tetragonal	mono-dimetrisch
2 u. 2 gliedrig oder 1 u. 1 axig.	prismatisch	orthotyp	rhombisch	holoedrisch rhombisch	trimetrisch
2 u. 1 gliedrig	prismatisch	hemiarthotyp	mono-klinoedrisch	hemiedrisch rhombisch	trimetrisch
1 u. 1 gliedrig	prismatisch	anorthotyp	tri-klinoedrisch	tetartoedrisch rhombisch	trimetrisch
3 u. 1 axig.		rhomboedrisch	hexagonal	hexagonal	mono-trimetrisch

Mitscherlich's Syst. hemianorthotyp diklinoedrisch.

phosphate of soda be present, the crystals exhibit a greater number of faces than those represented in *fig.* 111. According to Beudant again, a solution of alum or green vitriol mixed with finely pounded sulphate of lead, deposits in the paste which settles at the bottom a number of crystals having fewer and less polished faces than those obtained from pure solutions of the same salts: this effect is attributed by Beudant not so much to any mechanical influence exerted by the powder, as to the chemical action of the extremely small quantity of sulphate of lead which dissolves in the water. The peculiar forms of fluor-spar mentioned on page 13, likewise indicate the presence of foreign matter at certain times during its crystallization. In some cases only, as for example that of protosulphate of iron mixed with sulphate of zinc or sulphate of copper, has it been demonstrated that the foreign body separates from the solution along with the crystals; in most instances, on the contrary, *e. g.*, common salt with urea, this does not appear to be the case, and the action of these substances is perhaps for the most part attributable to the fact that their presence in the liquid from which the body crystallizes occasions the union of its particles according to fixed laws.

The rule that all the crystalline forms of any particular substance belong to the same system, and may be derived from the same ultimate form is subject to several exceptions; many substances, both simple and compound, are *dimorphous* and perhaps even *trimorphous*, *i.e.*, they present according to circumstances, 2 or 3 different groups of crystalline forms, which may be reduced to 2 or 3 different systems, or at least to 2 or 3 primitive forms. (*Vid.* Affinity.)

The number of systems of crystalline forms being small, while that of crystallizable bodies amounts to several thousands, it necessarily happens that a great number of bodies, differing widely in other respects come under one crystalline system; and, on the other hand, definite individual forms of the same system are found belonging to bodies of very different nature. If the forms of different substances belong to the regular system, there can be no difference in the magnitude of their angles, because the 3 axes of that system are equal: thus the angles of the regular octohedron remain the same, whether the crystals consist of alum, sal-ammoniac, or diamond. In the other systems, on the contrary, since the axes are unequal, and the inequality is of different magnitude in different substances, it follows that angular differences of various amount must exist in the crystals belonging to different bodies included in these systems. Thus the octohedron with a square base of Anatase (*fig.* 21), is acute, that of Zircon (*fig.* 23) obtuse, because in the former the longitudinal axis is longer, in the latter shorter than the lateral axes. These angular differences, however, are often very small: thus, for the blunt lateral edge of the rhombic prism of sulphate of magnesia, we find ($u : u'$ *fig.* 71) 90° 30′; in sulphate of zinc ($u : u'$ *fig.* 73) 91° 7′: and the angle of the terminal edges of the obtuse rhombohedron ($r : r'$) amounts in calcspar to 105° 5′, in manganese spar to 106° 51′, in iron spar to 107° 2′, in bitter spar to 107° 22′, and in calamine to 107° 40′. This near approach to equality in the angles is, however, often co-existent with similarity of chemical constitution. (*Vid.* Isomorphism, under the head of Affinity.)

Internal Structure, Texture of Crystals.

Almost all crystals may be more easily split or *cloven*, in certain directions lying in determinate planes, than in others; they exhibit from

1 to 7 *planes of cleavage* (Blätterdurchgänge) intersecting one another at determinate angles. This different facility of separation of a crystalline mass in certain directions may be shown not only by mechanical, but also, according to Daniell (*Schw.* 19, 38 *u.* 194) by chemical means; for when masses of different substances having a crystalline structure but no determinate external form, are placed in a liquid which does not act too rapidly on them, the undissolved portions sometimes exhibit grooves and depressions in the directions of the planes of cleavage, sometimes assume with tolerable distinctness the primitive forms of the systems to which the bodies belong. Again, when pieces of native sulphuret of antimony (Grauspiess-glanzerz) are placed in recently fused sulphuret of antimony, and half melted, the unmelted portion assumes the form of distinct crystals. (Faraday, *Qu. Jour. of Sc.*, 1821: also *Schw.* 32, 481.) To this class of phenomena also belong the *Figures of Widmanstadt*, and the *Moiré metallique, i. e.*, certain figures corresponding to the planes of cleavage, which come to light when meteoric iron or tin-plate is acted upon by acids. The more distinct planes of cleavage of a body are generally parallel to the faces of one of the primitive forms of the system to which it belongs: the less distinct to other less important faces of the same system. Thus, fluorspar has 4 planes of cleavage corresponding to the 8 faces of the regular octohedron, or the 4 faces of the regular tetrahedron; the 3 planes of cleavage of heavy spar (*fig.* 49) are parallel to the faces *p*, *u*, and *u'* of the upright rhombic prism; the 3 cleavage planes of calcspar to the 6 *r*- faces of the obtuse rhombohedron (*fig.* 141), &c. In different crystals of the same substance, one or other of the less distinct cleavage planes is often wanting; those however which can be traced, always make the same angle with each other, whatever may be the outward form of the crystal. Different substances may present the same cleavage planes when they belong to the regular system: if, however, they belong to any other system, they always exhibit at least slight differences in the directions of their cleavage planes. Imagine a crystal to be cloven according to its most distinct cleavage planes, or according to them all; it will then be resolved into the so-called *Simple Molecules* (*Molécules intégrantes*), whose form is either a regular or irregular tetrahedron, a regular or irregular three-sided prism, or a parallelopiped. When the faces of a crystal do not run parallel to its principal cleavage planes (the so-called *Secondary Form*), it is possible, by splitting the crystal at certain points, in directions parallel to these planes, to remove an external envelop, the so-called *Secondary mass*, and leave in the middle a crystalline kernel or *Nucleus*, whose faces are parallel to the principal cleavage planes. This form is regarded by Hauy (*Traité de Minéralogie*, T. 1), as the *Primitive Form*, which he supposes to have been developed first: he further supposes that on the faces of this primitive form there have been deposited successive laminæ consisting either of simple molecules or of aggregations of the same into compound molecules (*molécules soustractives*); and that these, being deposited in such a manner that the dimensions of the laminæ go on decreasing from one of the edges or summits, have produced the secondary form. This, however, is nothing more than a theoretical view, of which Hauy availed himself in calculating the arrangement of the secondary faces, since it is found that crystals on their first appearance exhibit the same form as after their complete development. Moreover Weiss has shown that independently of any such unnatural hypothesis, the angles of the different primitive and secondary faces of a crystal may be calculated from the mere proportion of its

linear dimensions. The atomic theory seeks to explain the structure of crystals by attributing a distinct form either to the atoms themselves, or if these be regarded as spheres, to aggregations of several of them. (*Vid.* Affinity.) The advocates of the dynamic theory proceed partly from the hypothesis that every solid body differs from a fluid in this respect, that the cohesion of its particles is of different amount in different directions, and further, that in a crystal these directions extend through the whole mass in straight polar lines.

Adhesion.

That kind of attraction which acts at infinitely small distances only between bodies of different natures, giving rise to the union of these bodies into a heterogeneous whole called a *Mixture* or *Mechanical Combination*, which may in most cases be overcome by mechanical force.

It appears to be exerted between all kinds of matter, imponderable as well as ponderable, but in various degrees. [On the adhesion of imponderable bodies to ponderable bodies see the part of this work which treats of Imponderables.] Respecting the adhesion of ponderable bodies to one another the following cases must be distinguished:—

1. *Adhesion between elastic fluids.*

Diffusion of Gases.—All gases, even when under existing circumstances they do not enter into chemical combination, yet diffuse themselves through one another and form a uniform mixture, though their specific gravities may be very different and they may be kept externally at perfect rest. If, for example, two bottles be connected by an upright glass tube 10 inches long and $\frac{1}{10}$ inch wide, the upper bottle being filled with hydrogen, nitrogen, binoxide of nitrogen, or common air, and the lower with the heavier gas carbonic acid, or the upper with hydrogen and the lower with common air, nitrogen, oxygen or binoxide of nitrogen, a portion of the heavier gas will after a few hours be found in the upper bottle, and after two or three days both bottles will contain the two gases in the same proportion (Dalton, *Phil. Mag.* 24, 8). The same result was obtained by Berthollet (*Mém. d'Arcueil*, 2, 463) with a tube 10 inches long and $\frac{1}{5}$ of an inch wide placed in a cellar where no change of temperature could take place to set the gases in motion. When hydrogen was the gas contained in the upper vessel the two gases were found to be uniformly mixed in 1-2 days; but when air, oxygen, or nitrogen, was contained in the upper vessel and carbonic acid in the lower, several weeks elapsed before the mixture became perfectly uniform.

If a cylinder filled with any gas and placed in a horizontal position be made to communicate with the external air by means of a knee-shaped tube in such a manner that the end of the tube is directed downwards when the gas is lighter and upwards when it is heavier than the air, the gas will gradually escape from the cylinder, its place being supplied by the air. According to Graham,

Of 100 volumes of gas there disappeared,

Sp. gr.		In 4 hours.	In 10 hours.
1	Hydrogen	81·6	94·5
8	Light carburetted hydrogen	43·4	62·7
8·5	Ammonia	41·4	59·6
14	Olefiant gas	34·9	48·3
22	Carbonic acid	31·6	47·0
32	Sulphurous acid	27·6	46·0
35·4	Chlorine	23·7	39·5

From this it appears that gases escape the more quickly the lighter they are; and their expansive power or *diffusibility* probably varies in the inverse ratio of the square roots of their specific gravities. Thus 47 measures of hydrogen escaped in two hours, and the same volume of carbonic acid in 10. Now this proportion of 1 : 5 is nearly that of the square root of 1 (spec. grav. of hydrogen) to the square root of 22 (spec. grav. of carbonic acid.) (Graham.)

If the cylinder contain a mixture of 2 gases, the more diffusible of the two will escape in greater proportion into the air, and the less diffusible in smaller proportion than if each gas were contained in the cylinder alone. Thus of 50 measures of hydrogen and 50 of olefiant gas there escape in 10 hours 47·7 measures of the former and 12·5 of the latter: similarly 47 measures of hydrogen and 20 of carbonic acid; though in these cases the opening of the knee-shaped tube is directed downwards: further in 4 hours there escape 26·8 vol. of light carburetted hydrogen and 12·5 of carbonic acid, also 22·8 of light carburetted hydrogen and 18·6 of olefiant gas. If two bottles be connected together by a tube placed in a vertical position, the lower bottle being 7 times as large as the upper and filled with carbonic acid gas, while the upper one is filled with a mixture of hydrogen and olefiant gas in equal volumes, the upper vessel will after 10 hours be found to contain, besides carbonic acid, a quantity of olefiant gas whose volume is 4 times as great as that of the hydrogen still remaining; the latter has therefore, in spite of its greater levity, diffused itself through the lower vessel with greater rapidity. (Graham, *Qu. Jour. of Sc.* 6, 74; also *Schw.* 57, 215).

In the same manner also vapours diffuse themselves through one another and through the more permanently elastic fluids.

When different elastic fluids have once diffused themselves uniformly through one another they never separate again according to their different specific gravities, for however long a time the mixture may be left at rest; this was shown long ago by Priestley.

These gaseous mixtures differ essentially from all other mixtures in the following respects: their heterogeneous constitution cannot be detected by the eye; they transmit light without the slightest disturbance; and they cannot be decomposed by mechanical means. It must be observed however that gases when devoid of colour cannot be distinguished from one another by the eye; they are invisible, and a glass vessel presents the same appearance whether it is exhausted of air or filled with a colourless gas. When therefore two gases have by their natural adhesion diffused themselves through each other with that extreme uniformity which their great mobility and lightness render possible, it is not to be expected that their heterogeneous nature should be detected by the eye; and even the colour which some gases possess is by this extremely intimate mixture so much divided that even the microscope cannot distinguish the coloured and colourless particles of gas. This minute division also causes the rays of light to be uniformly refracted in the gaseous mixture and to go straight through: lastly the same cause must prevent mechanical separation, unless we can find sieves fine enough to let the smaller particles pass through them and stop the rest. This peculiarity of gaseous mixtures has led several chemists to propose the following theories —which however are likely to be soon forgotten—respecting their nature.

1. Berthollet, Murray, and others regard a gaseous mixture as an imperfect chemical combination. Gas-mixtures are however destitute of all the characters of a chemical combination excepting uniformity: (*a.*)

It is not true that every substance can combine with every other: *e. g.* water mixes with alcohol but not with oil; on the contrary, every gas whether simple or compound mixes with every other; and the rapidity with which the mixture takes place depends not on the chemical nature of the gases, but only on their specific gravities. (*b.*) Agreeably to this theory Berthollet regards the evaporation of water and other bodies in the air below their boiling points as a chemical solution. But the quantity of any salt which water can dissolve increases with the quantity of water present; on the contrary, the quantity of water which evaporates in a given space is the same, whether the space be void of air or filled either with rarefied or condensed air: and the evaporation goes on most slowly in the last mentioned case, precisely that in which the quantity of the so-called solvent, the air, is the greatest. (*c.*) The mixing of gases is never attended with alteration of temperature, a phenomenon which always accompanies real chemical combinations. (*d.*) In most chemical combinations an alteration of volume takes place, but not in the mixing of gases. (*e.*) The refractive power of a gaseous mixture is, according to Biot and Arago, exactly the mean between the refractive powers of the individual gases which compose it; such however is not the case with real chemical combinations of gases, *e. g.* of hydrogen and nitrogen producing ammonia. (*f.*) Change of colour is often observed in chemical combinations, never in the mixing of gases. (*g.*) When one body is combined with another, a third body may withdraw the first and unite it to itself, the combination taking place less easily in most cases but more easily in some than if the first body were in the free state. Thus sulphur takes oxygen from protoxide of nitrogen at a higher, but from nitric acid at a lower temperature than from oxygen gas; but this substance takes fire in a mixture of oxygen and nitrogen (atmospheric air) at exactly the same temperature as in pure oxygen gas. Alkaline sulphites abstract oxygen from the air as easily as from pure oxygen gas, but not from protoxide of nitrogen which is a true chemical compound of oxygen and nitrogen. That phosphorus enters into slow combustion in the air at a lower temperature than in oxygen gas is accounted for by the more rarefied condition of the oxygen in the air.

2. Dalton supposed that in elastic fluids every atom of ponderable matter is surrounded with a sphere of heat: an elastic fluid is therefore to be regarded as a collection of spheres of heat each having a ponderable atom in its centre. His first hypothesis was that the calorific spheres belonging to the same elastic fluid repel each other, but not those of any other elastic fluid, so that as far as any other such fluid is concerned they may be regarded as not existing. Hence, neglecting the atoms of ponderable matter, which moreover are supposed to occupy an exceedingly small space, an elastic fluid may be regarded as a vacuum with respect to other elastic fluids: hence it is that bodies of this nature diffuse themselves rapidly through one another. To this it may be replied: (*a*) that experience shows that this diffusion when it takes place through narrow connecting tubes occupies several days, whereas according to the hypothesis it ought to be instantaneous; (*b*) that this supposed expansion of the gases ought to be attended with reduction of temperature; (*c*) that according to this hypothesis the atoms of the gases must often be brought into immediate contact, and consequently must combine when they have any affinity for each other: such however is not the case with the greater number of elastic fluids.

Dalton therefore afterwards assumed that the spherules of different

gases and vapours universally repel each other. He explained their mixture by supposing their spherules to be of different sizes, so that when they come in contact the different spherules press upon each other unequally and produce currents till the whole has become uniformly mixed. If however we calculate the size of the spherules on this hypothesis, but according to more accurate experiments, we find that all elastic fluids may be divided into 7 classes according to the magnitude of their gaseous spherules: if the volume of the gaseous spherules of sulphur-vapour be assumed equal to 1, that of oxygen gas, olefiant gas, phosphorus vapour, &c., will be 3, of hydrogen, nitrogen, and chlorine gases, &c., 6, that of hydrochloric acid gas, ammoniacal gas, &c., 12, and that of some others 9, 18, and 24. According to this hypothesis gases which belong to one and the same class and therefore have spherules of equal magnitude ought not to mix. Comp. Draper (*Phil. Mag. J.* 13, 241).

Mixture of gases likewise takes place when they are separated by the interposition of a porous body. In this more complicated case we have to consider, besides the various diffusibilities of the gases: (1.) The smallness of the pores which may favour the penetration of one gas rather than of the other. (2.) The different degrees of adhesion which the diaphragm exerts upon the different gases, by virtue of which the gas which adheres most powerfully penetrates the diaphragm most easily, and attaining the opposite surface, mixes with the other. (3.) The different degrees of affinity of the diaphragm for the gases (*e. g.* of water in a wet bladder) by which the gases are absorbed and carried to the other side of the diaphragm. The following cases require particular notice:

Cracks in Glass. Hydrogen gas, kept in a cracked receiver standing over water, escapes by degrees through the crack into the surrounding air, the water under the receiver rising to the height of $2\frac{2}{3}$ inch above the outer level. The remaining hydrogen contains 7 per cent. of nitrogen but no oxygen. If the receiver be filled with oxygen and nitrogen instead of hydrogen, nothing will escape from it. In the same manner hydrogen escapes out of bottles closed even with well ground stoppers, if the stoppers are not greased. (*Döbereiner, Ueber neu entdeckte höchst merkwürdige Eigenschaften des Platins, Jena*, 1825, s. 15.) The crack must be neither too narrow, in which case it would allow no hydrogen to pass, nor too wide, in which it would give passage to other gases as well; it often becomes too wide during the experiment from unequal pressure of the air. If the cracked receiver containing the hydrogen be placed over a trough of mercury and covered with an uncracked receiver containing air or carbonic acid, the mercury will rise in the inner receiver to the height of an inch or two, and sink in the same proportion in the outer; but when the difference of level amounts to about 2 inches, the air begins to enter through the crack. If the inner cracked receiver be filled with air and the outer with hydrogen, the mercury will rise in the outer and sink in the inner, proving that the hydrogen makes its way through the crack in opposition to its smaller specific gravity. (Magnus, *Pogg.* 10, 153.) Supposing it to be established that the remaining hydrogen is free from all traces of air or carbonic acid, which however is questioned by Graham who supposes that an interchange takes place, then these experiments would show that the smaller atoms of hydrogen are capable of making their way through intervals which are impervious to the larger atoms of carbonic acid, &c.

Bottles filled over mercury with detonating gas (a mixture of 1 vol. of

oxygen and 2 of hydrogen) to $\frac{4}{5}$ of their bulk, closed with well ground but ungreased stoppers, and inverted in mercury in such a manner that the level of the liquid may be somewhat lower without than within, and kept in a dark place for 15 months, are found still to contain the same volume of gas, $\frac{4}{5}$ of their bulk, but this gas is a mixture of about equal parts of detonating gas and common air. An interchange of gas and air has therefore taken place both between the glass and mercury at the outer and inner surface of the bottles and likewise through the intervals between the necks and stoppers. (Faraday, *Qu. J. of Sc.* 22, 220; also *Pogg.* 8, 124; and *Kastn. Arch.* 9, 398.)

Earthenware, Unglazed Wedgewood-ware. When gases are generated in earthen retorts or conducted through earthenware tubes, portions of them escape through the pores and are replaced by air entering from without, or when the earthen vessels are placed in the fire, by nitrogen and carbonic acid gases. If we heat in an earthen retort,—which when immersed in water is impervious to air blown into it but pervious under the stronger pressure produced by the air-pump,—water, hydrate of lime or moist clay, either to redness or but just above the boiling point of water, very little water is evolved from the retort, the greater part escaping through the pores; but there is obtained a quantity of atmospheric air amounting sometimes to $\frac{9}{10}$ of the weight of the water present and containing less oxygen and more carbonic acid (obtained from the fire) than common air. If the retort is enclosed in a receiver standing over mercury, the neck together with the gas-delivery tube passing airtight through an opening in the top, and heat is applied to the retort by means of a large lens, a considerable quantity of air is disengaged, water collects over the mercury and the mercury rises $3\frac{1}{2}$ inches if the retort is made of compact earthenware, to a smaller height if it is more porous, the air of the receiver penetrating into the retort apparently in opposition to the laws of hydrostatics. If the receiver contains hydrogen or binoxide of nitrogen instead of common air, the mercury rises in like manner and these gases issue from the gas-delivery tube. From the same cause, when vapour of water is passed through a tobacco-pipe tube heated to redness, a mixture of gases is obtained differing little from common air. Vessels or tubes of chalk or white marble act in the same manner as earthenware vessels. (Priestley, *Exper. and Obs.* 3, 29.) When black oxide of manganese is heated in a Wedgewood-ware retort and the resulting gas collected in separate portions, the first portion contains 22, the second 25, the third 26, the fourth 44·75, the fifth 44, the sixth 46·5, the seventh 41, and the eighth 18·25 per cent. of oxygen. The earlier portions are contaminated with the air of the vessel, the latter with the mixture of nitrogen and carbonic acid gases which penetrate into the retort, the quantity of this mixture continually increasing with the enlargement of the pores by the heat, (and with the increased diffusibility of the gases consequent upon expansion, *Graham*). Pfaff. (*Schw.* 18, 80.) This mixing of gases through earthenware explains the incorrect results of certain old experiments, in which vapour of water was said to be converted into nitrogen gas by passing it through red-hot tubes, and chloride of silver to be reduced by heating it in retorts with dry charcoal.

Gypsum. If one end of a glass tube be closed with gypsum-paste, and after the gypsum has dried and hardened, the tube be filled with any gas, its open end plunged under mercury and its closed end exposed either to the air or to an atmosphere of any other gas contained in a receiver, the inner gas will escape and the outer enter the tube, in quan-

tities which are inversely as the square roots of their densities. Thus 3·87 measures of hydrogen which escape from the inner tube are replaced by 1 measure of atmospheric air. Now putting the density of air = 1, that of hydrogen is 0·0668; the square roots of these numbers are 1 and 0·2623; and 0·2623 : 1 = 1 : 3·87 nearly. Diffusion also takes place though very slowly through flexible dolomite, coal, wood, and dry cork. (Graham, *Phil. Mag. J.* 2, 175, 269 and 351; abstr. in *Pogg.* 28, 331); also, *Elements of Chemistry* 1, 83. Thomson's observations thereupon. (*Phil. Mag. J.* 4, 321.)

Caoutchouc. A sheet of caoutchouc tied over the opening of a wide-mouthed bottle full of hydrogen gas, is soon pressed inwards even to bursting. If the bottle be filled with air and placed in an atmosphere of hydrogen, the swelling and bursting take place outwards. A well closed bottle of caoutchouc perfectly empty does not distend when placed in hydrogen gas: but if it contains a small quantity of air distension takes place. Almost all gases excepting nitrogen exhibit the same relations towards common air as hydrogen does, but in different degrees; they all penetrate caoutchouc with various velocities in order to mix with air. In order to measure these various velocities, a sheet of caoutchouc is tied over the shorter funnel-shaped arm of a siphon-tube, mercury is poured into the other arm which is made very long, so that a portion of air may remain between the mercury and the caoutchouc, and the shorter arm introduced under a receiver standing over the mercurial trough and filled with the gas to be examined. The gas penetrates the caoutchouc, mixes with the air and increases its volume; consequently the mercury in the longer arm is driven upwards, sometimes to the height of 63 inches, and might be driven higher if the caoutchouc could sustain a greater pressure without bursting. By experimenting in this manner on different gases, it is found that the same volume of ammoniacal gas obtains access to the air in 1 minute, as of sulphuretted hydrogen in 2½′, of cyanogen in 3½′, of carbonic acid in 5½′, of protoxide of nitrogen in 6½′, of arseniuretted hydrogen in 27½′, of olefiant gas in 28′, of hydrogen in 37½′, of oxygen in an hour and 53′, and of carbonic oxide in 2 hrs. 40′ Caoutchouc appears from this to absorb gases with different degress of facility; of carbonic acid it absorbs its own volume and swells up in consequence. (Mitchell, *J. Roy. Inst.* 2, 101.)

Animal Membranes. A moist bladder or moistened gold beaters'-skin acts like a sheet of caoutchouc. (Mitchell.) A moist bladder two-thirds filled with coal-gas or air, swells when suspended in carbonic acid gas and finally bursts. In this experiment as much as 40 per cent. of carbonic acid sometimes mixes with the coal-gas, while only a very small quantity of the latter escapes into the atmosphere of carbonic acid. Hence the water of the moistened bladder absorbs carbonic acid and gives it up again on the inner side. (Graham, *Qu. J. of Sc.* 6, 88; also *Schw.* 57, 227; extr. in *Pogg.* 17, 347.) A perfectly dry bladder containing air does not distend in carbonic acid gas: a bladder moderately wetted expands to a greater extent than one which is thoroughly soaked; for the thinner the film of water which absorbs the gas, the sooner will the gas reach the opposite surface. If the bladder containing air be moistened with alcohol (which absorbs carbonic acid more readily than water does) it will expand in an atmosphere of carbonic acid as quickly as if it were moistened by water—but not more so: the alcohol likewise causes it to shrivel and soon destroys its power of transmitting gases. Rubbing the bladder with oil of anise or olive oil (neither of which absorbs carbonic acid) prevents the

expansion. A wet bladder containing air expands more quickly in sulphuretted hydrogen than in carbonic acid: after being distended as far as possible in the last-mentioned gas, it will expand still further if placed in an atmosphere of sulphuretted hydrogen; whereas, if exposed to the air it will regain its original size. A bladder containing air also expands when immersed in water holding carbonic acid in solution, but not so quickly as in an atmosphere of the gas. A fish's air-bladder expands under the above-mentioned circumstances more quickly than a urinary bladder: on the contrary, this property is not exhibited by the lining membrane of a fowl's egg or by curried sheepskin: the latter allows air and carbonic acid to pass through it with equal facility. (Baumgartner, *Zeitschrift Ph. Math.* 8, 9.) These experiments show that gases cannot be preserved in bladders without alteration. If a piece of bladder be tied over the upper and widened end of a glass tube, the tube then filled with water and its lower end plunged under mercury, the mercury will rise within it to the height of 3 inches, in consequence of the water penetrating the bladder and escaping into the air: but as soon as this height is attained the pores of the bladder allow air to pass through them and the further rise of the mercury is prevented. (Magnus, *Pogg.* 10, 157.) According to Fischer (*Pogg.* 11, 130) who perhaps made use of a stronger bladder, the mercury may attain the height of 12 inches or even more; it ultimately reaches to the bladder itself, the whole of the water evaporating and leaving nothing but a slimy residue. If a tube sealed at top and tied over with a piece of bladder at the bottom be filled with water and exposed to the air, the bladder will be pressed inwards in consequence of the evaporation of the water and air will enter, not however in bubbles, but dissolved by the water: the air thus introduced collects at the upper end of the tube on the gaseous form, and finally all the water evaporates and the tube becomes filled with air. (Fischer.)

2. *Adhesion of elastic fluids to solids.*

1. Wood and other solid bodies immersed in water or other liquids appear covered with air-bubbles.

2. The close adhesion of a thin film of air and vapour of water to the surfaces of glass tubes is the cause of the difficulty of obtaining barometers and thermometers free from air. This thin film of air and vapour cannot be removed by the air-pump, but only by boiling the mercury, the vapour of which, as it escapes, carries the air and aqueous vapour along with it. That unboiled mercury is free from air and water, and therefore has nothing to do with the difficulty in question, is shown among other proofs by this; that when mercury is boiled in a narrow barometer-tube having a large bulb at one end, and the tube inverted in a basin of mercury and inclined, then if the quantity of boiled mercury be not sufficient to fill the bulb, but in consequence a considerable quantity of unboiled mercury must enter it, the barometer, on being set upright again, will stand at the same height as before. (Bellani, *Brugn. Giorn.* 16, 20.)

3. This power possessed by solid bodies of fixing elastic fluids on their sufaces, is much increased when the extent of surface is enlarged by pulverizing. All pulverized bodies are more or less hygroscopic, *i. e.*, they become covered, on exposure to the air even though it may be very dry, with a film of condensed vapour of water, and also of condensed air, by which their weight may be increased some 3 or 4 per cent. Many bodies seem to possess the property of condensing the oxygen of the air on their surfaces in preference to the other gases contained in it.

3. *Adhesion between liquids.*

1. The spreading of water over the surface of mercury seems to arise chiefly from this cause.

2. When one liquid is very intimately mixed with another, both being perfectly transparent when separate, a turbid and often milky fluid, called an *Emulsion*, is produced, out of which the two bodies separate slowly in obedience to their different specific gravities;—*e. g.*, distilled water overcharged with a volatile oil.

4. *Adhesion between liquids and solids.*

1. If a plate of any solid body be placed in contact with the surface of a liquid, a certain force, determinable by weight, is required to separate them. Experiments of this kind are described by Guyton Morveau, in the *Encyclopédie Méthodique*, Paris, 1786. (An instance of the combined action of cohesion and adhesion is afforded by the holding together of two glass plates having a film of water or oil between them.) Liquids attach themselves to solid bodies, even in opposition to their own weight and cohesion, and rise along their surfaces, *e. g.*, the concave surface of water in glass vessels; writing; painting; the rise of liquids in capillary tubes; blotting-paper; the rope-pump. The height to which the liquid rises for a given distance between the walls of the solid body affords a measure of the force of adhesion. Earthen vessels filled with water holding carbonate of soda in solution and charged under strong pressure with carbonic acid gas, exhibit the following phenomena according to the degree in which they have been fired:—(*a.*) Well, but not thoroughly burnt.—The water holding the carbonate of soda in solution is by the pressure of the carbonic acid gas gradually and completely driven through the pores of the vessel; on opening the vessel after it has become thoroughly dry, the gas escapes with violence. Hence water passes more easily through very narrow pores than carbonic acid gas, because the atoms of the latter are surrounded with spheres of heat. (*b.*) From vessels still less burnt the gas escapes while the whole or the greater part of the liquid remains behind: for when the pores are sufficiently large, the gas, being the more moveable body, escapes more quickly than the water. (*c.*) If the vessel has been but very slightly baked, the gas and liquid escape together, the latter in the form of fine rain or mist, as long as the pressure of the gas is sufficient to force it out. (Jeffrey, *Phil. Mag. J.* 16, 10.) Cracks produced in the sealed end of a glass tube by heating and then wetting it with water, may be of four degrees of fineness. (*a.*) The widest allow water to escape when the tube is exposed to the air. (*b.*) Those somewhat narrower only when immersed in water. (*c.*) Still narrower cracks are pervious only when the liquids within and without the tube are of different chemical nature and disposed to combine; no rising of the liquid takes place as in endosmose; no evaporation of water takes place on exposing the crack to the air. (*d.*) Cracks of yet greater fineness are permeable only under the following galvanic conditions: the tube contains a solution of nitrate of silver with a platinum wire immersed in it, the outer vessel containing water with a zinc wire; the zinc and platinum are in metallic contact; under these circumstances a portion of silver is deposited on the platinum wire, in the course of 24 hours, and the water is found to contain a very small quantity of nitrate of zinc. (N. Fischer, *Pogg.* 11, 132.)

3. When a solid body in a state of minute division is diffused through

a liquid by any mechanical or chemical force, it becomes *suspended* in consequence of its adhesion to the liquid, and often separates but very slowly. The separation of the suspended body—(*a*) by leaving the whole to stand, and then pouring off the liquid from the sediment at the bottom, or drawing it off with a siphon, is the process of *Subsidation* and *Decantation*; (*b*) by combining it with a third body so as to form larger and nonsuspendible masses, that of *Clarification;* (*c*) by pouring the liquid through a finely porous substance, which perhaps acts by adhesion on the suspended body, that of *Straining* or *Filtration.*

4. *Endosmose.* When two liquids capable of mixing are separated by a porous diaphragm, each of them permeates the diaphragm in order to mix with the other. This exchange, however, always takes place in unequal proportions, so that the volume of the one liquid increases while that of the other diminishes; but some portion of the latter always goes over to mix with the former. The stronger current is called by Dutrochet, *Endosmose,* the weaker, *Exosmose;* the increasing liquid, therefore, is said to exhibit endosmose, that is to say, the other liquid goes into it. This unequal penetration is mainly attributable to the different degrees of adhesion exerted by the diaphragm on the two liquids; that which on account of stronger adhesion, enters the diaphragm with greater facility, will sooner reach the opposite surface and there be taken up by the other liquid. Difference of viscosity may also have something to do with the effect. Experiments on this subject are usually made by placing a glass tube or inverted filter closed at the bottom by a diaphragm and filled with one of the liquids, in a vessel which contains the other, both liquids being made to stand at the same height. The level then rises either in the inner or the outer vessel, according to the nature of the liquid; if the two currents are of the same strength, the level remains unaltered, although the fluids become uniformly mixed. The observations made upon this phenomenon, arranged according to the nature of the diaphragm, are as follows:—

a. Baked earthenware. Endosmose proceeds from water to solution of sulphurous acid of 1·02 sp. gr. to dilute sulphuric acid of 1·054 sp. gr., and to sulphuretted hydrogen water: on the contrary it proceeds at all degrees of temperature and concentration from oxalic and tartaric acid to water. (Dutrochet.)

b. Caoutchouc. Through any material covered with caoutchouc endosmose proceeds from alcohol to water, first slowly, but afterwards quickly, when the caoutchouc has been acted upon by the alcohol; at the same time the alcohol becomes more and more dilute by the action of an opposite stream of water. (Dutrochet.) A caoutchouc bottle filled with ether gradually empties itself in alcohol or water; if filled with alcohol it distends in ether but empties itself in water: if filled with water it distends when placed either in alcohol or in ether. Hence caoutchouc is most pervious to ether then to alcohol, and lastly to water. (Mitchell, *J. Roy. Inst.* 2, 112, and 317.)

Bladder. Endosmose proceeds at 10° C. from water to dilute sulphuric acid of 1·093 sp. gr.: but in the contrary direction with sulphuric acid of 1·054 sp. gr. It also proceeds from solution of sulphurous acid of 1·02 sp. gr. to water; both these acids, however, soon destroy the bladder, and then the two liquids reassume the same level. (Dutrochet.) Solution of sulphuretted hydrogen goes over to water according to Dutrochet; but according to Mitchell the exchange takes place without alteration of volume. At 10° C. hydrochloric acid of 1·017 sp. gr. remain

n equilibrium with water; if the acid is stronger, *e.g.* 1·02, the water oes over to it; if weaker, *e.g.* 1·015, it goes to the water; at 22° C. it ust be diluted to 1·002 sp. gr. in order that endosmose may be directed om it to water. (Dutrochet.) At 10° C. nitric acid of 1·09 sp. gr. emains at the same level as water; if the sp. gr. be 1·12 or higher, the ater goes to the acid; at 1·08 sp. gr. and under, the acid goes to the ater. (Dutrochet.) Solution of oxalic acid goes over to water at all egrees of temperature and concentration; the more it is concentrated the aster it travels: on the contrary, it filters through the bladder much more owly than pure water (the slowness increasing with the concentration) the lower surface of the bladder be placed in contact with a solution of e same strength as that whose rate of filtration is to be determined. his seems at variance with the supposition that endosmose is due to dif- rence of adhesive power. A solution of 11 parts of tartaric acid in 100 water (sp. gr. 1·05) remains in equilibrio with pure water at 25° C.; ith a stronger solution the principal current is directed from the water the acid; with a weaker, from the acid to the water. At 15° C. equi- brium takes place with a solution of 21 parts of tartaric acid in 100 of ater (sp. gr. 1·1); and at 8° with 30 of acid to 100 water (sp. gr. 1·15); d at + 0·25° with 40 acid to 100 water (sp. gr. 1·21). It appears, herefore, that the tendency of the acid to go over to the water increases s the temperature is lowered. A solution of 11 parts of citric acid in 00 parts of water (sp. gr. 1·05) equilibrates with water just like a solu- ion of tartaric acid. (Dutrochet.) Endosmose proceeds from water to olutions of saltpetre and common salt. A solution of common salt of ·12 sp. gr. rises in water twice as high in the same time as a solution of ·06 sp. gr. A solution of common salt of 1·085 sp. gr. goes over to a olution of Glauber's salt of the same density. (Dutrochet.) Endosmose proceeds from water to solutions of common salt, chloride of calcium, protosulphate of iron and sulphate of copper. The alteration of level eases when the liquids in both vessels become of the same strength. With common salt the rising of the liquid is much less rapid than with e more soluble chloride of calcium. If the experiment be made with o solutions of the same salt of different degrees of concentration, dosmose always proceeds from the weaker to the stronger. So like- ise from the solution of a less soluble salt, such as sulphate of potash, to saturated solution of a more soluble salt such as acetate of potash. Magnus, *Pogg.* 10, 160.) Endosmose proceeds from water to solutions all kinds of salts, increasing in force with the strength of the solution; is strongest with chloride of copper; then follow green and blue vitriol; en common salt and sal-ammoniac; it is weak with chloride of iron and lphocyanide of potassium: with protochloride of tin, nitrate of silver, d chloride of gold, which are decomposed by the bladder, no endosmose observable. (N. Fischer, *Pogg.* 11, 126.) If the outer vessel contains solution of sulphate of copper, the inner one water having a piece of on in it, endosmose is directed to the water provided the iron touches e bladder, while copper is deposited on the outer surface of the bladder, d acid and oxygen carried over to the iron by galvanic action. (Fischer, *ilb.* 72, 305, Magnus.) Zinc causes the water to rise as well as iron, t more slowly; if the iron does not touch the bladder the water sinks. ach. *Schw.* 58, 20.)

A bladder tied over a glass filled with alcohol, swells up under water such an extent, that when the bladder is pricked with a needle, the cohol spirts out in a long stream. (Parrot, *Pogg.* 10, 166.) In this

experiment a little alcohol also passes into the water. (Magnus.) It follows, therefore, that alcohol and water exhibit contrary actions towards bladder and caoutchouc, because alcohol adheres more strongly to caoutchouc, water to bladder; water containing sulphuretted hydrogen penetrates into alcohol even more quickly than pure water. (Mitchell.)—For similar experiments by Sömmering see *Alcohol*.—Water passes to ether in the same manner as to alcohol. (Dutrochet.) Endosmose is directed from water to solutions of glue, gum, sugar, and white of egg; and when these liquids have the same density, 1·07, the rise of the liquid is measured in the case of glue by 3, of gum by 5, of sugar by 11, and of white of egg by 12: the last exhibits, therefore, the strongest endosmose. A solution of 1 part of gum in 16 of water passes over to a solution of 1 part of sugar in 16 or even 32 of water, although the former solution is much more viscous than the latter. If 1 part of oxalic acid is mixed with the solution of 1 of sugar in 16 of water, the endosmose is from the sugar solution to the pure water: when 2 parts of sugar and 1 of oxalic acid are dissolved in 16 of water the solution remains in equilibrium with pure water, portions of sugar and oxalic acid passing however into the water. A solution of sugar rises 3 times as high with solution of oxalic acid as with pure water in the same time; it acts in the same manner towards solutions of tartaric and citric acids. (Dutrochet.)

d. Stem of the Allium Porrum (*leek*). Endosmose from water to sulphuric acid of 1·0274 sp. gr. to solution of sulphuretted hydrogen, oxalic acid and tartaric acid of various degrees of concentration and at various temperatures; in the contrary direction, therefore, to that with bladder. (Dutrochet, *Ann. Ch. Phys.* 35, 393; 37, 191; 49, 411; 51, 159; extr. in *Pogg.* 138; 12, 617; 28, 359; also *Ann. Chim. Ph.* 60, 337.)

5. *Adhesion between Solids.*

1. Fine dust adheres to vertical and inverted horizontal surfaces.

2. Two heterogeneous bodies with very finely polished surfaces adhere together with a certain force. *Comp.* Prechtl. (*Pogg.* 15, 223.)

3. This kind of adhesion is most powerfully manifested when one of the bodies is first brought to the liquid state (by which it acquires the power of adapting itself perfectly to the surface of the other), and afterwards solidified. This is the principle of glueing, pasting, soldering, silvering of mirrors, the use of mortars, cements, &c.

PART I.

GENERAL CHEMISTRY,

OR

THEORY OF AFFINITY IN GENERAL.

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Synonymes: *Chemical Attraction, Chemical Force, Elective Attraction, Elective Affinity, Chemische Kraft, Verwandtschaft, Wahlverwandtschaft, Wahlanziehung, Affinitas, Attractio Electiva, Affinité.*

History. Chemical combination was in early times attributed to the general principle of Hippocrates that like assorts with like: hence the word Affinity (Verwandtschaft) which seems to have been first employed by Barchhusen. Becher assumed, in accordance with this dogma, that when two bodies are capable of combining they must contain a common principle. Others, among whom was Lemery, supposed that solvents are furnished with a number of sharp points by means of which they are more or less adapted to insinuate themselves into the pores of solid bodies and combine with them. According to Stahl's theory, chemical combination proceeds from the intimate approximation of the parts of the combining bodies but not exactly in the manner of a wedge. Newton was the first who referred chemical combination to the principle of universal attraction, though he at the same time partly assumed that this attraction between ultimate particles is not exactly the same as that which acts between the great bodies of the universe. Geoffroy the elder, in 1718, drew up the first Table of Affinity, which was subsequently enlarged and corrected by Bellert, Wenzel, Bergman and Guyton-Morveau. The idea that many chemical combinations take place in definite proportions only had occurred to some of the older chemists, *e.g.*, Wenzel, Bergman, Kirwan; and they endeavoured to determine these proportions. This view was confirmed by Richter, Proust, Gay-Lussac, Dalton and Berzelius, and expanded into the *Theory of Definite Proportions* or *Stoichiometry.*

I. Fundamental Notion of Affinity.

Affinity is that kind of attraction by virtue of which bodies of dissimilar nature combine together into a whole which appears perfectly uniform to the senses, even when assisted by the most powerful instruments. The act of union is called *Chemical Combination**, the resulting product a *Chemical Comopund*, and if it be fluid, a *Solution.* The dis-

* The term *Combination* is sometimes also applied to the resulting product: the corresponding German word *Verbindung* is applied indiscriminately to the act of combination and to the product. [W.]

similar substances contained in the compound are its *Components* or *Elements*; and of these if one be fluid and the other solid, the former is called the *Solvent* or *Menstruum*, the latter the *Dissolved body* or *Solutum*.

The sphere of action of chemical affinity has by some chemists been too much enlarged, by others too much contracted. An instance of the former of these errors has already been given in speaking of the mixture of gases (page 21). The following views on the contrary appear to restrict the idea of a chemical compound between too narrow limits.

1. Many combinations of liquids with gases in which the latter lose their gaseous condition are by Dalton and others regarded as mechanical (vid. *Water*).

2. All mixtures of liquids one with another, and all solutions of solids in liquids, are by Berzelius, Mitscherlich, Dumas, and others of the most distinguished modern chemists, regarded as not chemical, unless they take place in definite proportions: *e g.*, mixtures of water and alcohol, alcohol and volatile oil; solutions of acids, alkalies and salts in water, alcohol, &c. Mitscherlich attributes such combinations to adhesion, Berzelius to a modification of affinity,—while, according to his view, chemical combinations properly so called result not from affinity but from electrical attraction. Dumas ascribes them to a *solvent power* which he supposes to hold a middle place between cohesion and affinity: inasmuch as the former causes the union of bodies of the same nature, the latter that of bodies of very opposite natures, producing compounds possessed of new and peculiar properties; while the solvent power causes the combination of bodies of very similar nature, as of metals with metals, acids, alkalies and salts with water, resin and fat with alcohol, &c. These views lead to no satisfactory definition of Affinity (for objections to them, vid. *Gehler's Phys. Wörterbuch.* Ausg. 2, 9, 1862). They are nevertheless true in this respect that a distinction must be made between strong and weak affinities, the former producing compounds of definite constitution and characterised by distinct and remarkable properties, while the latter gives rise to products of less definite composition and differing less in their properties from the bodies of which they are formed: on this ground Berthollet, in an earlier state of the science, distinguished the more intimate combinations as *Compounds* (*Combinaisons*) and the less intimate as *Solutions* (*Dissolutions*), though the two classes merge into one another by imperceptible gradations and admit of no determinate separation.

II. Range of Affinity.

Every simple, *i.e.*, hitherto undecomposed body, is capable of entering into chemical combination with others, but generally speaking not with all. It is possible that every simple substance may have affinity for every other; but many compounds of these substances may not have been obtained hitherto, because the components have not been placed under the particular conditions in which their affinity can exert itself; others it may be impossible to form because the affinity between their components is overcome by the force of gravitation, cohesion, or elasticity. For example, the fact of carbon not combining with mercury may perhaps be explained partly by the great cohesion of carbon, the tendency of its particles to remain combined amongst themselves being possibly greater than their inclination to unite with those of mercury; partly from the greater specific gravity of mercury, by which that substance is prevented from diffusing itself through so comparatively light a body as carbon.

So likewise the elasticity of nitrogen may prevent that substance from combining with metals, inasmuch as by entering into such combination, it would lose its gaseous form. If a gas be regarded as a compound of a ponderable body with heat, the explanation just given will amount to this,—that nitrogen is prevented from combining with metals in consequence of its greater affinity for heat.

Compounds resulting from the union of two simple substances or *Compounds of the First Order*, to which belong the inorganic acids, bases, metallic chlorides, &c., are themselves for the most part capable of combining—sometimes though rarely—with simple substances, but much more frequently with other compounds of the same order. In this manner are formed *Compounds of the Second Order*, the most important of which are the simple salts. These compounds again are capable of uniting both with each other and with compounds of the first order, thus forming compounds of the higher orders: and so on. But the more complicated the constitution of any such substance may be, the more nearly will the combining tendencies of its elements be satisfied, and the less therefore will be the inclination of those elements to enter into further combinations. In this manner chemistry reaches its limit. In compounds of the second order, a distinction may be made between *Proximate* and *Ultimate elements* (*Principia proxima et remota*); in those of the third order, between *Proximate elements of the first order*, *Proximate elements of the second order* and *Ultimate elements*. Thus in sulphate of potash, sulphuric acid and potash are the proximate elements; and since sulphuric acid consists of sulphur and oxygen, potash of potassium and oxygen, we say that oxygen, sulphur and potassium are the ultimate elements. Since compounds generally exhibit affinities different from those of their components, it follows that the affinities of the components in their character of primitive or elementary substances will sometimes differ from the resulting affinity of the compound. The older chemists distinguished such cases by particular names. Thus if there be a substance A with which another substance B is capable of uniting, while a third substance C is not capable by itself of entering into such combination but becomes so by uniting with B, the affinity thus manifested was called *Mediating Affinity* (*vermittelnde Verwandtschaft, Affinitas approximans, appropriata s. adjuta.*) For instance, alumina (C) by combining with sulphuric acid (B) becomes soluble in water (A). If neither B nor C can combine with A, but the combination BC can form such a union, the affinity is called *Produced* or *Developed Affinity*, (*erzeugte Verwandtschaft, Affinitas producta*). Thus neither carbon nor nitrogen can combine with mercury; but their compound, cyanogen, has a powerful affinity for it. An example of the instability of four liquids to combine is afforded by the so-called *four elements* (mercury, solution of carbonate of potash, dilute alcohol and rock-oil).

III. Formation of Chemical Compounds.

The case in which 2 or more bodies combine without causing the destruction of any previously existing chemical compound was called by the older chemists *Affinity of composition* or *of mixture*, *zusammensetzende* or *vermischende Affinität*, *Affinitas compositionis s. mixtionis.*

1. *Conditions under which Chemical Combination takes place.*

A. The affinity of the combining bodies must be sufficient to overcome all opposing forces, such as gravitation, cohesion, and elasticity.

B. The substances must be brought into immediate contact, for affinity does not act at sensible distances.

C. Generally speaking, one at least of the combining bodies must be either in the liquid or gaseous state, and if it be not so at ordinary temperatures it must be brought into that state by elevation of temperature.

Hence the old rule: *Corpora non agunt nisi fluida* from the erroneous supposition that the fluid or *menstruum* was the only active body, and the solid or *solvendum* a resistance to be overcome. Solid bodies either do not combine at all, or their combination is attended with great difficulty, because from the immobility of their particles their points of immediate contact are but few, and the exceedingly thin film of compound which may be formed at such points acts as a partition to prevent further contact and consequently further combination. But by continued rubbing, which renews the points of contact, more complete combination may often be effected: in this manner finely divided copper may be made to combine with sulphur, the combination being even attended with rise of temperature. If, on the other hand, the compound formed by the two solids is itself fluid, its mobility gives rise to continually renewed contact, and combination goes on. Thus ice under 0° unites with chloride of sodium and other salts, and solid amalgam of lead with solid amalgam of bismuth. Crystallized oxalic acid and lime may be made to combine by rubbing them together, because the acid contains more water of crystallization than the oxalate of lime produced is able to take up: hence at the beginning of the action a little water is set free and dissolves the oxalic acid, &c., &c. In some cases it is sufficient to heat one of the solid bodies till it softens: thus iron surrounded with charcoal and heated to whiteness is slowly penetrated by the charcoal (*Cementation*). When in consequence of one or both bodies being in the fluid state, combination takes place at the ordinary temperature or a little above it, it is called *Solution in the wet way*, (*Solutio via humida*); if a higher temperature is required, the process is called *Solution in the dry way*, *Fusion* (*Solutio via sicca*, *Confusio.*)

D. Even if one or both of the bodies be in the fluid state, a higher temperature is often necessary to effect the combination.

Melted sulphur will not combine with carbon; the sulphur must be brought in the state of vapour into contact with red-hot charcoal, although the elasticity of the vapour might rather be expected to interfere with the combination. Neutral carbonate of soda in the efflorescent state absorbs carbonic acid very slowly at first, but more and more quickly as it gets heated by the absorption, and ultimately with great violence. (Mohr, *Ann. Pharm.* 29, 268.) Charcoal requires to be heated before it will burn in oxygen gas, that is, before it will combine with the oxygen. At ordinary temperatures, oxygen may be mixed with hydrogen and other inflammable gases without combining with them, but at a red heat combination takes place immediately. In this case both bodies are fluid, and we might expect that heat by increasing their elasticity would rather oppose than favour the combination. The manner in which heat acts in such cases is not precisely understood. If for instance we suppose that the affinity between oxygen and hydrogen in the cold is not sufficient to overcome their elasticity but becomes greater at a higher temperature, then the resulting compound ought, on cooling, when the affinity between its elements is again diminished, to be resolved into those elements by the action of elasticity. If again, with Monge and Berthollet, we suppose that the portion of the gaseous mixture first heated presses by

expansion on the neighbouring particles, and thereby causes them to combine, it may be argued on the other hand that such pressing together of the particles can have but little effect, and that no combination ensues when the gaseous mixture is gradually subjected to a pressure of 50 or even 150 atmospheres.

E. In some cases, light has the same effect as an elevation of temperature.

Chlorine and hydrogen or carbonic oxide.

F. Electricity likewise favours the combination of many substances, acting chiefly by elevation of temperature, but also by the compression which the electric spark exerts upon the gaseous mixture through which it passes.

G. In some instances, the expansion of gaseous bodies favours their combination with others. Phosphorus undergoes slow combustion in oxygen gas however low the temperature may be, the action going on more quickly as the gas is more rarefied; a mixture of oxygen and non-inflammable phosphuretted hydrogen gases explodes on expansion.

H. The presence of a heavy solid body, particularly a metal, having a great extent of surface, likewise causes, sometimes at ordinary, sometimes at slightly elevated temperatures, the combination of oxygen with inflammable gases and vapours, which would otherwise take place only at a red heat.

This property is most strikingly exhibited by platinum; the more finely divided the platinum, the stronger is its action. When the combination of oxygen with inflammable gases takes place at its surface, the heat developed raises its temperature and thereby increases its activity, till at length the metal becomes red-hot and then sudden combination ensues. (*Vid.* Oxygen and Hydrogen.) Platinum appears to condense gases particularly oxygen on its surface by adhesion (page 26), so that the heterogeneous atoms, being deprived of their heat-spheres, are able to approach one another and combine.

I. Many bodies, particularly those which are very elastic, or very cohesive, combine together only when aided by the chemical co-operation of other bodies.

a. Formation of chemical compounds by *Substitution.*

One, or both, of the combining bodies is previously contained in another compound which is less elastic or less coherent than the body itself, and from which it passes over to the new combination in the so-called *nascent state*, before it has time to reassume the highly elastic or highly coherent state which belongs to it. Nitrogen and hydrogen will not combine to form ammonia by the action of either heat or electricity; but if tin-filings be placed in contact with water and binoxide of nitrogen, the tin will rob both these bodies of their oxygen, and the hydrogen disengaged from the water will combine at the moment of liberation with the nitrogen set free from the nitric oxide, and form ammonia. Tin acts in the same manner on dilute nitric acid. Ammonia is also produced on heating nitre with gum, and likewise from azotized organic substances when heated alone. Oxygen and nitrogen will not, without great difficulty, combine directly to form nitric acid: this substance is however obtained when ammoniacal gas is passed over red-hot oxide of manganese, or a mixture of ammoniacal gas and oxygen passed through a red-hot tube. The nitrogen being the less elastic of the two elements of ammonia, is more disposed to combine with oxygen when the hydrogen has been separated from it by the action of that substance, than when it

is in the free state. Similarly the combinations of nitrogen with chlorine, bromine, iodine, sulphur, and phosphorus are not obtained directly from nitrogen gas itself, but from the decomposition of ammonia. Iodine will not combine directly with oxygen gas to form iodic acid: this acid is however produced on heating iodine with nitric acid. Similarly iodic acid is produced, as also bromic and chloric acid (which latter cannot be formed by means of nitric acid) by bringing iodine, bromine, or chlorine in contact with solution of potash. The compound of water and oxygen, called peroxide of hydrogen, is obtained not from water and oxygen gas, but from water, peroxide of barium, and hydrochloric acid, the acid abstracting baryta and leaving the excess of oxygen of the peroxide of barium to go over to the water.

Among the instances in which cohesion is diminished by the action of a pre-existing compound, the following may be mentioned: Anhydrous baryta does not absorb carbonic acid gas, but the hydrate takes it up readily, water being set free at the same time. Crystallized alumina (Sapphire), and many other weak bases in the crystallized or ignited state do not dissolve in hydrochloric acid; but after being heated with a large quantity of caustic potash with which they combine, they become soluble in that acid. If the insolubility of crystallized alumina arose from its cohesion being greater than its affinity for the acid, it ought not to dissolve in the acid after being ignited with potash, but to separate, in consequence of its greater cohesion, after the potash had been dissolved in the acid: it appears then to be only the peculiar kind of aggregation belonging to the crystalline state that prevents the alumina from acting in obedience to its affinity for the acid.

b. Induction of chemical combination by *communication of chemical energy.*—A body in the act of chemical combination has the power of inducing the same kind of activity in another body and causing it to combine with a third body, thereby forming a compound which, under the existing circumstances, would not have been formed without the presence of the first body. (Liebig, *Ann. Pharm.* 30, 262.) Wet peat-earth gradually absorbs oxygen gas; if the latter be mixed with hydrogen, a portion of the hydrogen enters into combination with the oxygen, which it would not do in the absence of the peat-earth. (Saussure.) Nitrogen gas does not by itself combine with oxygen, even when heated; but if a mixture of nitrogen and hydrogen be set on fire, the hydrogen burns, producing water, and a portion of the nitrogen combines at the same time with oxygen, producing nitric acid. Pure copper does not oxidate in water mixed with sulphuric acid, but when combined with zinc and nickel (in German silver), metals which decompose acidulated water, or when combined with three times its weight of zinc only, it oxidates and dissolves completely together with the other metals. Platinum when alone does not oxidate and dissolve in nitric acid, but when alloyed with silver it becomes soluble in that acid.

2. *Circumstances and Results of the chemical combination of Ponderable Bodies.*

A. Emission and absorption of imponderable substances.

In all cases of the combination of ponderable bodies, a change and generally a rise of temperature is produced, sometimes amounting to the most intense heat. This rise of temperature is generally greater in proportion to the strength of the affinity by which the combination is brought

about; a fall of temperature is less frequent. (*Vid.* Heat.) Some combinations are attended with a slight development of electricity. (*Vid.* Electricity.)

B. Time in which combination takes place.

a. With the same two bodies, the rapidity of combination is increased by diminishing the quantity of a solid body in proportion to that of a liquid, or of a gaseous body in proportion to that of a liquid or a solid; by diminishing the cohesion of a solid by heating, or the elasticity of a gas by cooling and compression; and lastly, by comminuting a solid body and increasing the number of points of contact by agitation and friction.

A salt placed at the bottom of a quantity of water dissolves very slowly when at rest, because the heavy film of saline solution which is gradually forming remains above the salt and prevents its contact with the rest of the water: the same salt placed at the upper part of the water in a muslin bag or a filter dissolves very rapidly, because the solution as it is formed sinks to the bottom and allows the rest of the water to come in contact with the salt. Ammoniacal gas directed upon the surface of water is very slowly absorbed, because the new compound (solution of ammonia) is lighter than water, and therefore forms a layer on the surface preventing the further contact of the water and gas; but if the gas is directed through a tube to the bottom of the water, the absorption takes place very quickly. Hydrochloric acid gas, on the contrary, is rapidly absorbed when directed on the surface of water because its solution in that liquid being heavier than water sinks to the bottom, and fresh water comes to the surface. A metal slowly cooled after fusion dissolves more rapidly in acids than it would if it had been hammered.

b. With different bodies, the rapidity of combination is greater, in proportion as their affinity is greater, their cohesion less, their difference of specific gravity smaller, their diffusion through one another more easy, and the fluidity of the new compound more complete. The combination of solids with fluids takes place much more slowly in consequence of the greater cohesion of the former than that of fluids with fluids. Liquids of different specific gravity combine slowly when at rest and disposed one above the other in layers, but quickly when shaken. Gases combine most quickly of all, because they diffuse themselves through each other spontaneously by adhesion (page 20). If the new compound is solid at ordinary temperatures, it places itself between the new bodies and hinders their further combination; *e. g.*, zinc and sulphur.

C. Proportions in which bodies combine.

This forms the subject-matter of *Stoichiometry, or the Doctrine of Chemical Proportions or Chemical Equivalents.*

Ponderable bodies generally combine in definite proportions, which come out with greater distinctness as the affinity between the combining substances is stronger. With respect to the proportion in which two bodies combine, the following cases present themselves:

a. Two bodies may be mixed in any proportion whatever, and in no case does the mixture present any peculiar properties: e. g., Water and alcohol, alcohol and ether, ether and volatile oils.

b. One body A may take up any quantity whatever of another body B; but B, after having combined with a certain quantity of A, takes up no more of it.—B is then said to be *saturated* with A; the *point of satu-*

ration is attained; a *saturated combination* or *solution* has been formed. 1 part of linseed-oil may be dissolved in 40, 1000 parts or any greater quantity of alcohol; but when 30 parts of alcohol have taken up 1 part of linseed-oil, any greater quantity remains undissolved and forms a milky liquid on agitation. 10 parts of common salt mixed with any quantity of water greater than 27 pts. will form a clear solution; but if common salt be added by small portions at a time to 27 parts of water, the first 10 pts. will dissolve completely, but any further quantity will remain undissolved. Similar relations are exhibited by water, alcohol and ether towards many salts and other solid bodies, and likewise towards gases. Water and ether agitated together in equal quantities separate when left at rest into two layers; the lower consists of water saturated with $\frac{1}{10}$ ether, which may be replaced by any quantity of water whatever; the upper is ether holding a very small quantity of water in solution, and miscible with ether in all proportions.

In most of these cases the point of saturation varies with the temperature and external pressure. Most solid bodies dissolve more abundantly in fluids the more the temperature is raised, probably on account of diminished cohesion; but as exceptions to this law we find that lime and some of its salts dissolve more abundantly in cold than in warm water, and 10 pts. of common salt saturate 27 of water at all temperatures. Under increased pressure, liquids will dissolve larger quantities of gaseous bodies; moreover Perkins found (*Ann. Ch. Phys.* 23, 410, also *Schw.* 39, 361) that a milky mixture of alcohol with a larger quantity of bergamot oil than it can dissolve at the ordinary pressure of the air, became perfectly limpid from solution of the oil under a pressure of 1100 atmospheres.

c. Two bodies combine in one or a small number only of definite proportions, subject to no variation from temperature or outward pressure.

This law, the most important of all, holds good in all cases in which the more powerful affinities are concerned. It implies a mutual saturation of A with B, and B with A.

α. The two bodies A and B combine in one proportion only. In this case the same relative quantities ensure the saturation of A with B, and of B with A.

Chlorine and hydrogen combine only in the proportion by weight of 35·4 : 1; zinc and sulphur only as 32·2 : 16.

β. The two bodies combine in 2 definite proportions only: A is saturated with B at one of these proportions, and B with A at the other.

Six parts of carbon combine with 8 pts. of oxygen to form carbonic oxide, with 16 to form carbonic acid; in carbonic oxide the oxygen is saturated with carbon, in carbonic acid, the carbon is saturated with oxygen; for 8 oxygen will not take up more than 6 carbon, nor 6 carbon more than 16 oxygen; moreover between carbonic oxide and carbonic acid there exists no intermediate combination containing more than 8 and less than 16 of oxygen united with 6 of carbon. It is true that carbonic oxide and carbonic acid gases may be mixed in any proportion whatever and thus a gas obtained in which 6 parts of carbon are present in connection with more than 8 and less than 16 of oxygen: but this is no chemical compound, but a mere mixture of gases, from which potash will remove the carbonic acid and leave the carbonic oxide behind. Similarly 35·4 chlorine with 101·4 mercury form corrosive sublimate, and with 202·8 mercury they form calomel: a substance, which for every 35·4 pts. of chlorine contained more than 101·4 and less than 202·8 mercury, would

be a mixture of corrosive sublimate and calomel, from which alcohol would dissolve the former and leave the latter.

γ. The two bodies combine in 3, 4, or 5 distinct proportions.—In this case the combination of A with the largest quantity of B, gives one point of saturation, and that of B with the largest quantity of A, the other; between these two points of saturation are situated 1, 2, or 3 intermediate combinations. But here, as in the former case, there is no gradual transition from the minimum to the maximum, but a sudden passage from one characteristic combination to another.

48 molybdenum with 8 oxygen form molybdous oxide, with 16 oxygen, molybdic oxide, and with 24 ox. molybdic acid. 16 sulphur with 8 oxygen form hyposulphurous acid; with 16 ox. sulphurous acid with 20 ox. hyposulphuric acid; and with 24 ox. sulphuric acid. 14 nitrogen with 8 oxygen form nitrous oxide; with 16, nitric oxide; with 24, nitrous acid; with 32, peroxide of nitrogen or hyponitric acid; and with 40 of oxygen, nitric acid. Many intermediate compounds may be regarded as combinations of two saturated compounds in definite proportions. Thus, 103·8 lead form with 8 oxygen (the smallest possible quantity) the yellow, with 16 oxygen (the greatest) the brown oxide of lead: between these is found the red oxide, which contains 103·8 lead with $10\frac{2}{3}$ oxygen, or (multiplying by 3) 311·4 lead with 32 oxygen, and may be regarded as a compound of yellow oxide, 2 (103·8 lead + 8 oxygen) and brown oxide (103·8 lead + 16 oxygen). Moreover, the red oxide is decomposed by acetic acid, which dissolves out the yellow oxide, leaving the brown. Similarly, magnetic iron ore may be regarded as a compound of protoxide and peroxide of iron.

These more intimate and definitely proportioned compounds considered under *c*, are subject to the two following important laws.

First Law relating to the same two bodies. Suppose two bodies A and B to be capable of uniting in several proportions; then if the smallest quantity of B which can combine with a given quantity of A, be multiplied either by $1\frac{1}{3}$, or by $1\frac{1}{2}$, or by 2, or by $2\frac{1}{2}$, or by 3, 4, 5, or any higher whole number, the products will give the other quantities of B, which may combine with the before mentioned given quantity of A. (Berzelius.) Thus 6 carbon combine with 8 and 2.8 oxygen; 16 sulphur with 8, 2.8, $2\frac{1}{2}$.8 and 3.8 oxygen; 14 nitrogen with 8, 2.8, 3.8, 4.8 and 8 oxygen; 103·8 lead with 8, $1\frac{1}{3}$.8 and 2.8 oxygen. This law affords a check on the results of experiment: thus if experiment had indicated that carbon unite with 8 oxygen to form carbonic oxide, and with 15·5 oxygen to form carbonic acid, it might have been suspected, since 15·5 is not one of the multiples of 8 by $1\frac{1}{3}$, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3 . . . . , that the composition either of carbonic oxide, or of carbonic acid, or of both, had not been correctly determined by experiment.

Second Law, relating to different bodies. From the proportion which A combines with B on the one hand and with C on the other, may likewise be calculated the proportion in which combination may take place between B and C. If, for example, experiment shows that 1 part of A combines with 3 parts of B and with 8 parts of C, then B and C must combine either in the proportion of 3 B to 8 C, or in some other proportion in which the 3 B are multiplied by one of the following numbers, $1\frac{1}{3}$, 2, $2\frac{1}{2}$, 1, 3, 4, 5, &c., or the 8 C by one of the same numbers, or the 3 B by one and the 8 C by another number of the same series. The same law holds good in the case of any number of bodies, so that if 1 A will combine with 3 B, 8 C, 10 D, 12 E, &c., then B will combine with C, D and

E either in the proportion of 3 : 8, 3 : 10, 3 : 12, or else in proportions obtained by multiplying one or each of these numbers by some factor taken from the above-mentioned series. Taking sulphur for the body denoted by A, we find that 16 sulphur with 103·8 lead form sulphuret of lead; with 24 oxygen, sulphuric acid; with 1 hydrogen, hydrosulphuric acid; with 3 carbon, bisulphuret of carbon; and with 13·6 iron, iron-pyrites. Now 103·8 lead combine, not with 24 oxygen, but with 8 oxygen to form yellow oxide of lead; the 103·8 lead must therefore be multiplied by 3 to give the proportion in which lead and oxygen are combined in the yellow oxide. Oxygen and hydrogen combine, not in the ratio of 24 : 1, but of 8 : 1 or 24 : 3; the 1 hydrogen must therefore be multiplied by 3.—24 oxygen combine not with 3 carbon, but with 18 carbon in carbonic oxide: the 3 carbon has therefore to be multiplied by 6.—24 oxygen combine not with 13·6, but with 81·6 iron to form protoxide of iron, the latter number being equal to 6 times 13·6.

From these two laws it follows that to every simple substance there belongs a certain relative weight, according to which it combines with given relative weights of other simple substances, only that in many cases this relative weight requires to be multiplied by some number of the series already mentioned. This determinate relative weight of a body is by those who admit the atomic theory, called the *Atomic Weight;* by those, on the other hand, who either reject this theory altogether, or regard it as not sufficiently established,—the *Combining Weight, Chemical Weight, Chemical Equivalent, Combining Proportion, Equivalent Proportion,* or *Equivalent Number, Stoichiometrical Proportion,* or *Stoichiometrical Number.*

The origin of these two laws is most satisfactorily explained by the atomic theory (which we shall hereafter develop more completely), according to which every simple substance consists of very small invisible particles called *atoms,* these atoms being of uniform weight and volume in each individual substance, while the atoms of different substances may be of different weight and volume. It is assumed that in chemical combination the heterogeneous atoms lay themselves close together, and so form *compound atoms,* which, when collected into a mass, constitute the new compound: further, that the atoms have a tendency to unite in simple numerical proportions: *e. g.,* 1 atom of A with 1, 2, 3, or more atoms of B; or 2 atoms of A with 3 or 5 atoms of B, or 3 atoms of A with 4 atoms of B. It is only in organic compounds that more complex proportions occur.

If we now examine the preceding examples according to this view, we may assume that the absolute weight of an atom of carbon is to that of an atom of oxygen = 6 : 8, and that 1 At. carbon combines either with 1 At. oxygen to form carbonic oxide, or with 2 At. oxygen to form carbonic acid. It will then follow that in carbonic oxide every 6 parts by weight of carbon are combined with 8 parts of oxygen, and in carbonic acid, every 6 parts of carbon with 16 of oxygen.—We may also with great probability assume that the atomic weight of sulphur is twice as high as that of oxygen, and therefore = 16, if that of oxygen be taken = 8. Since now, according to experiment, 16 parts of sulphur can combine with 8, 16, 20 or 24 parts of oxygen, it follows that 1 At. sulphur combines with 1, 2, $2\frac{1}{2}$ and 3 At. oxygen; and since half atoms are inadmissible, the combination of 16 sulphur with 20 oxygen (= 32 : 40) may be regarded as consisting of 2 At. sulphur combining with 5 At. oxygen.—If the atomic weight of nitrogen be taken equal to 14, it will be found that 1 At. nitrogen can combine with 1, 2, 3, 4 &

5 At. oxygen.—The atomic weight of lead being assumed equal to 103·8, the yellow oxide of lead must be supposed to contain 1 At. lead with 1 At. oxygen, the brown oxide 1 lead with 2 oxygen, and the red oxide 3 lead with 4 oxygen. Thus it is explained why the smallest quantity of B with which A will combine, must be multiplied by $1\frac{1}{3}$, $1\frac{1}{2}$, 2, $2\frac{1}{3}$, 3, 4, and other whole numbers, to find the other proportions. For 1 At. of A takes up sometimes 1, sometimes 2, sometimes more atoms of B, and hence the augmentation proceeds according to whole numbers: or 2 At. of A unite with 3 or 5 of B: hence arises multiplication by $1\frac{1}{2}$ or $2\frac{1}{2}$; or 3 At. A with 4 At. B, whence multiplication by $1\frac{1}{3}$.

With respect to the second law, we have the following. If experiment shows that 1 part of A combines with 3 parts of B, and with 8 parts of C, then on the supposition that in these compounds 1 At. of A exists in connexion with 1 At. of B, and with 1 At. of C, it follows that the atomic weights of A, B, C, = 1 : 3 : 8; since, however, in these combinations, 1 At. of A may be combined with 2, 3, 4, or any greater number of atoms of B or C, or 2 At. of A with 3 or 5 At. of B or C, or 3 At. of A with 4 At. of B or C, &c. &c.; or finally, since B and C must not be supposed always to combine in equal numbers of atoms,—it will often be necessary, in determining the equivalent numbers according to which B and C combine, to multiply the 3 parts of B or the 8 parts of C, or both of them, by one of the numbers in the series $1\frac{1}{3}$, $1\frac{1}{2}$, 2, $2\frac{1}{3}$, 3, 4, 5, . . .

Atomic Weights of Simple Substances.

Of the *absolute weight of atoms* we can know nothing, excepting that they must be extremely small. It is only the relative weight of the atoms of different bodies that can be determined with any degree of probability from the proportions by weight according to which the bodies combine. This *relative atomic weight* may be discovered by assuming arbitrarily a particular number to represent the atomic weight of any one substance, and then determining the atomic weights of the other bodies according to the proportions by weight in which they combine. Some chemists, following Dalton, put the atomic weight of hydrogen, because it is the smallest, = 1; but the greater number agree with Berzelius in assuming oxygen = 100. The former method is to be preferred, because it gives simpler numbers and thereby favours the retention of them in the memory and facilitates calculation. The atomic weights of many other bodies appear to be simple multiples of that of hydrogen, and consequently when hydrogen is taken = 1, they are represented by whole numbers; e.g., carbon 6, oxygen 8, nitrogen 14, sulphur 16, &c. These numbers likewise contain one digit less than the others: thus, oxygen 8 instead of 100, carbon 6 instead of 75, nitrogen 14 instead of 175, sulphur 16 instead of 200, &c. This simplicity, moreover, obtains particularly with regard to those substances of which the innumerable organic compounds are formed. In favour of the other method it is indeed advanced that oxygen is of all the elementary bodies that which forms the widest range of compounds, and consequently that calculation must be facilitated when that element is expressed by such round numbers as 100, 200, 300, 400, 500, &c., but the numbers 8, 16, 24, 32, 40, are more quickly written, and encumber the addition so much the less as the other elements of the compound are at the same time expressed by simpler numbers. Moreover hydrogen occurs in a great number of inorganic compounds, especially in the form of water; and in organic compounds it

occurs more frequently, and in greater numbers of atoms than oxygen, so that it makes a very great difference in the calculation whether this substance is denoted by 1 or by 12·50.

The atomic weight of one body being arbitrarily fixed, *e.g.*, that of hydrogen = 1, the atomic weights of other bodies are found as follows: 100 parts of water contain, according to experiment, 11·111 hydrogen and 88·889 oxygen. If now it be assumed as most probable that in water every atom of hydrogen is in combination with 1 atom of oxygen, then the weight of 1 At. hydrogen must be to that of 1 At. oxygen = 11·111 : 88·889 = 1 : 8. If 100 grains of water contain x atoms of hydrogen, and therefore (according to the hypothesis that in water every 1 At. hydrogen is combined with 1 At. oxygen) also x At. oxygen, then x At. hydrogen must weigh 11·111 grains, and x At. oxygen 88·889 grains: if then the weight of x At. hydrogen is to that of x At. oxygen = 11·111 : 88·889, then likewise the weight of 1 At. hydrogen must be to that of 1 At. oxygen = 11·111 : 88·889 = 1 : 8. 100 parts of sulphuretted hydrogen contain 5·9 parts of hydrogen and 94·1 parts of sulphur: if now we assume that this compound contains equal numbers of atoms of hydrogen and sulphur, we have the proportion, 5·9 : 94·1 = 1 : 16, or the atomic weight of sulphur is 16 if that of hydrogen be assumed = 1. Further, on examining the relation of sulphur to oxygen we find that 100 parts of sulphurous acid contain 50 of sulphur and 50 of oxygen; and 100 parts of sulphuric acid, 40 sulphur and 60 oxygen. Now 50 : 50 = 16 : 16, and 40 : 60 = 16 : 24; and since the atomic weight of sulphur is 16, that of oxygen 8, we may conclude that in sulphurous acid 1 At. sulphur = 16 is combined with 2 At. oxygen = 16, and in sulphuric acid with 3 At. oxygen = 24. Since carbonic oxide contains 6 parts of carbon combined with 8 oxygen, and carbonic acid 6 carbon with 16 oxygen, we estimate the atom of carbon at 6, and suppose that in carbonic oxide it is combined with 1, and in carbonic acid with 2 atoms of oxygen. Sulphuret of carbon contains 6 parts of carbon united with 32 sulphur; therefore 1 At. carbon with 2 At. sulphur. Similarly the atomic weight of nitrogen is estimated at 14, because 14 parts of nitrogen combine with 8, 16, 24, 32, and 40 parts oxygen: consequently 1 At. nitrogen, with 1, 2, 3, 4, and 5 At. oxygen. In ammonia 14 parts of nitrogen are combined with 3 of hydrogen, therefore 1 At. nitrogen with 3 At. hydrogen. Since in yellow oxide of lead (massicot) 103·8 lead are combined with oxygen, the atomic weight of lead may be estimated at 103·8; according to this, galena, which is composed of lead and sulphur in the proportion of 103·8 : 16, must be regarded as containing equal numbers of atoms of its elements. Th[e]n, then, the atomic weight of hydrogen being assumed = 1, the followi[ng] atomic weights have been determined: oxygen 8, sulphur 16, carbon [6], nitrogen 14, lead 103·8; and in a precisely similar manner the atom[ic] weights of the other elements are calculated.

If, on the other hand, the atomic weight of oxygen be assum[ed] = 100, the numbers just found will be altered as follows: since 8 : 1 = 100 : 12·5, the atomic weight of hydrogen, which was 1 in the form[er] system, will in the present be 12·5. Similarly we shall find that t[he] atomic weight of sulphur is (8 : 16 = 100 : x) = 200: of carbon (8 : 6 = 100 : x) = 75: of nitrogen (8 : 14 = 100 : x) = 175; and of lead (8 : 10[3·8] = 100 : x) = 1297·5. Generally, the atomic weights obtained by assuming that of hydrogen = 1 must be multiplied by 100 and divided by 8, in order to find the corresponding atomic weights on the suppo[sition]

tion of 1 At. oxygen = 100: conversely, the latter atomic weights are reduced to the former by multiplying by 8 and dividing by 100. However the atomic weights obtained on the latter supposition may differ from those resulting from the former, it is evident that the ratio of the numbers remains the same, and, since all the magnitudes are relative, this difference of the atomic weight is only apparent.

Another less obvious cause of difference in the determination of atomic weights is as follows. Just as the atomic theory itself rests only on a probable hypothesis, so likewise the assumption that certain compounds contain equal, others unequal numbers of heterogeneous atoms must be regarded as merely probable. For example it cannot be proved that in water every atom of hydrogen is united with exactly one atom of oxygen; there may be 2 or more atoms of hydrogen combined with each atom of oxygen, or one atom of hydrogen with 2 or more atoms of oxygen—and similarly with regard to all other compounds. The hypothesis of Davy, Wollaston, and W. Henry, that water contains equal numbers of atoms of oxygen and hydrogen has been assumed above as the more probable: but the majority of chemists agree with Berzelius in supposing that it contains 2 atoms of hydrogen for each atom of oxygen. On this supposition 1 At. oxygen will be not 8 but 16 times as heavy as 1 At. hydrogen, so that if the atomic weight of hydrogen = 1, that of oxygen = 16; and if the atomic weight of oxygen = 100, that of hydrogen = 6·25: for according to this view, 1 At. oxygen = 16 combines with 2 At. hydrogen = 2.1 = 2; or 1 At. oxygen 100 combines with 2 At. hydrogen = 2.6·25 = 12·5. This view rests chiefly on the law laid down by Berzelius, viz. that *simple substances in the gaseous state contain equal numbers of atoms in equal volumes.* Since then in the formation of water 2 volumes of hydrogen combine with 1 volume of oxygen, and since according to the law just stated, 2 vol. hydrogen contain twice as many atoms as 1 vol. oxygen, it follows that in water every 2 At. hydrogen must be combined with 1 At. oxygen. If 1 cubic inch of hydrogen gas contains x At. hydrogen, then according to this law, 1 cub. in. oxygen gas will contain x At. oxygen; according to this, the atomic weights of the 2 bodies will be to one another as the specific gravities of the gases; for between x atoms of the two gaseous bodies there must exist the same proportion by weight as between 1 atom of each of them. The specific gravity of oxygen gas is 16 times as great as that of hydrogen, and therefore, according to this view, the atomic weight of oxygen must be 16 times as great as that of hydrogen; and in water 1 At. oxygen = 16 is combined with 2 At. hydrogen = 2.1 = 2; or 1 At. oxygen = 8 with 2 At. hydrogen = 2. $\frac{1}{2}$ = 1 if the atom of oxygen be represented by 8 and that of hydrogen by $\frac{1}{2}$.

In accordance with this law, Berzelius reckons the atomic weights of nitrogen, iodine, bromine, chlorine and fluorine at only half the value which from other considerations they appear to have. If the specific gravity of hydrogen gas = 1, that of oxygen is 16, of nitrogen 14, of iodine-vapour 126, of bromine vapour 78·4, of chlorine gas 35·4; hence according to Berzelius the atomic weight of oxygen is to those of these as 16 : 14 : 126 : 78·4 : 35·4 or = 8 : 7 : 63 : 39·2 : 17·7. In the case of fluorine, whose specific gravity in the gaseous state is not yet known, Berzelius has in the same manner, on account of its analogy with chlorine, reduced the atomic weight to one-half of that usually given.

Against this it must be alleged, (1) that we are by no means compelled to admit the above law, which on the contrary is in direct oppo-

sition to the results of experiments; and (2) that it obliges us to admit the existence of atoms smaller than those which occur in any known compound, or than is consistent with the manner in which they replace each other in different compounds,—and leads to the use of atomic numbers much larger than is necessary.

1. According to the atomic theory, every gas consists of ponderable atoms surrounded by spheres of heat. If now it be admitted that these heat-spheres have the same volume (external pressure and temperature being equal) in all ponderable substances, then it will follow that all gases must contain equal numbers of atoms in equal volumes. But that such a supposition is by no means necessary is seen at once from this,—that with respect to compound gases the law in question is sometimes true, sometimes false. Thus 1 volume of hydrogen gas and one volume of chlorine gas form 2 volumes of hydrochloric acid gas. If now we suppose x to be the number of atoms in each volume of the simple gases, then by the concurrence of all the individual atoms of hydrogen with all the individual atoms of chlorine, there will have been formed x atoms of hydrochloric acid, and these fill up the space of 2 measures: consequently the two measures of hydrochloric acid gas contain the same number only of atoms as 1 measure of hydrogen gas or 1 measure of chlorine gas: 1 atom of hydrochloric acid must therefore be surrounded by a heat-sphere twice as large as that which surrounds 1 atom of chlorine or 1 atom of hydrogen. This example (many others will afterwards appear) shows that the above law is not applicable to compound gases; indeed it was never applied to them. We see also from the same example that there is no necessity for admitting that the atoms of all *simple* substances in the gaseous state are surrounded by calorific envelopes or heat-spheres of the same magnitude; but just as in compound bodies these envelopes are of different magnitudes bearing simple relations to one another, so likewise may it be the case with simple substances; and we may therefore suppose that th[illegible] heat-spheres which surround an atom of hydrogen, nitrogen, iod[illegible] bromine, or chlorine in the gaseous state are twice as large as thos[illegible] oxygen, so that 2 measures of their gases will contain just the sa[illegible] number of atoms as 1 measure of oxygen gas. Finally, that this differe[illegible] of magnitude in the heat-spheres must be admitted even with regard simple substances, and consequently that the above law, with all the co[illegible] sequences deduced from it respecting the atomic numbers, must be ab[illegible] doned, is shown by the determination of the specific gravities of merc[illegible]ry and sulphur vapours. The atomic weight of mercury is usually given = 101·4 (oxygen = 8) and it is assumed that the red oxide contains 1, and the grey oxide 2 atoms of metal combined with 1 atom of oxygen: but according to Dumas the sp. gr. of mercury vapour is a little more th[illegible] 6 times that of oxygen gas: according to this the atomic weight of m[illegible]cury should be = 50·7 (oxygen = 8), and the red oxide of merc[illegible] should contain 2 and the grey oxide 4 atoms of metal for every atom of oxygen,—which last proportion is highly improbable. Again the atomic weight of sulphur is universally admitted to be double that of oxyge[illegible]; according to the above law then, the specific gravity of sulphur-vapour should be twice as great as that of oxygen gas; but the direct experiments of Dumas and Mitscherlich show that it is 6 times as great. It is out of the question to suppose, merely for this reason, that the atomic weight of sulphur is 6 times that of oxygen, viz. 48, when oxygen = [illegible]; the resulting proportions would be con[illegible] On account, notwithstanding the great den[illegible]

ht of sulphur is still universally admitted to be double that of gen: but in order to explain this departure from the law, it is assumed he adherents of that law that exceptions to it are more likely to occur apours than in the more permanent gases, and that sulphur in the of a heavy vapour is perhaps in a peculiar isomeric condition (for changes which sulphur undergoes when heated see *Amorphism*,) and if we could convert it into vapour without bringing it into this liar condition by heating, it would probably yield a lighter vapour. his it may be replied that the difference between vapours and gases is not of kind but only of degree, and the law, if true, must be equally icable to both; moreover that if the peculiar isomeric condition of hur in the state of vapour be admitted, we may expect that oxygen he state of gas will be in a similar isomeric condition, and will there- yield a gas twice as much condensed as that obtained from the ter number of elementary bodies. In short, the same unknown causes irtue of which 1 volume of sulphur vapour contains 6 times and 1 me of hydrochloric acid gas only half as many atoms as 1 volume of rogen gas, nitrogen gas, &c., may also effect that 1 volume of oxygen contains twice as many atoms.

. There is no compound containing but one atom of hydrogen, nitro- &c., as small as that adopted by Berzelius; neither does any known pound contain 3, 5, 7, &c., but always 2, 4, 6, 8, &c. of such atoms. makes the existence of such small atoms improbable and their tion superfluous and troublesome. According to Berzelius, if the ic weight of oxygen = 8, that of hydrogen must = $\frac{1}{2}$, of nitrogen , of iodine = 63, of bromine = 39·2, of chlorine = 17·7, and of ine = 9·37. But 39·2 potassium which unite with 8 oxygen, also with 2. 63 iodine, 2. 39·2 bromine, 2. 17·7 chlorine, and 2. 9·37 ine. Hence 2 atoms of these bodies are required to replace 1 atom ygen in combination with potassium; or 2 atoms of these bodies are *quivalent* of 1 atom of oxygen. If the atoms be supposed twice as the idea of an atom will coincide with that of an equivalent, and nfusion will be avoided. According to Berzelius's view, however, terms must often be distinguished one from the other. These con- tions have led Berzelius to introduce the notion of *double atoms*. uble atom of hydrogen, nitrogen, iodine, bromine, chlorine, and ne corresponds in his system to a single atom of these bodies as are considered in this work.

[For the reasons favourable to Berzelius's view founded on the specific of the elementary bodies, see the chapter on Heat.]

n the determination of atomic weights, the following principles are y useful as guides:

. Let it be granted that heterogeneous substances combine in the est possible numerical proportions, and let their weights be deter- l accordingly.—Thus, hydrogen being assumed = 1, and therefore en = 8, the most suitable number that can be given to sulphur is 16: At. sulphur will then combine with 1 At. hydrogen to form sul- tted hydrogen, with 1 At. oxygen to form hyposulphurous acid, 2 atoms to form sulphurous, and with 3 to form sulphuric acid, &c. atomic weight of sulphur were made = 48 according to the specific y of its vapour, then, instead of the preceding relations, we should, 1 At. sulphur combined with 3 hydrogen, and 1 At. sulphur with 3 9 oxygen.

. Let no atomic weights be admitted smaller than those which

actually occur in combinations. This principle is introduced with especial reference to the atomic weights of hydrogen, nitrogen, iodine, bromine, chlorine, and fluorine, adopted by Berzelius, but it is likewise of use with regard to phosphorus, arsenic, and antimony.

3. As a general rule, the total weight of the atoms composing an acid must be of such amount that the compound atom may just suffice for the saturation of one atom of a salifiable base.—Thus, 16 sulphur and 3.8 oxygen form 40 sulphuric acid, and 103·8 lead with 8 oxygen form 111·8 oxide of lead: now 40 sulphuric acid just satisfy 111·8 oxide of lead. If sulphur, on account of the specific gravity of its vapour, were made = 48, these 48 parts of sulphur with 72 of oxygen would form 120 sulphuric acid, and these would saturate 3.111·8 parts, therefore 3 atoms of oxide of lead. To this rule there are, however, certain unmistakable exceptions, which render it necessary to admit, not only *monobasic* acids, 1 atom of which saturates 1 atom of a base, but also bibasic, tribasic, and perhaps even quartobasic and quintobasic acids, 1 atom of which saturates 2, 3, or more atoms of a base.

4. When a metal combines with oxygen in one proportion only, to form a salifiable base, it is assumed, supposing that the laws of Isomorphism do not oppose the assumption, that the compound contains equal numbers of atoms of the metal and of oxygen.—Potash contains 1 At. potassium combined with 1 At. oxygen: yellow oxide of lead, 1 At. lead with 1 At. oxygen. When a metal forms a number of salifiable bases with different proportions of oxygen, the oxide which forms the strongest base is to be regarded as containing the metal and oxygen in equal numbers of atoms. The protoxide of iron is a stronger base than the peroxide. Now since in the former, 8 parts of oxygen are combined with 27·2 of iron, the atomic weight of iron, on the supposition that this oxide contains equal numbers of atoms of the metal and oxygen, = 27·2: in the peroxide 2. 27·2 iron are combined with 3 . 8 oxygen, or 2 At. iron with 3 At. oxygen. If the peroxide were supposed to contain equal numbers of atoms of iron and oxygen, the atomic weight of iron would be 18·1, and the protoxide would contain 3 At. iron with 2 At. oxygen. Again, the red oxide of mercury is a stronger base than the grey oxide. In the red oxide, 8 parts of oxygen are combined with 101·4 of mercury; in the grey oxide, 8 oxygen with 202·8 mercury. Accordingly the atomic weight of mercury must be estimated at 101·4, the red oxide containing 1 At. mercury, and the grey oxide 2 At. mercury combined with 1 At. oxygen. The case is precisely similar with the black and red oxides of copper, excepting that the atomic weight of copper is of different amount, viz., = 31·8. With the two oxides of tin the case is reversed, the lower oxide (59 tin + 8 oxygen) being the stronger, and the higher oxide (59 tin + 16 oxygen) the weaker base.

5. It is supposed that substances which closely resemble one another in physical and chemical properties, combine with a third body, according to the same number of atoms. If nickel combines with oxygen in the proportion of 1 : 1 and 2 : 3 At., this must also be the case with cobalt, which bears so very closely an analogy to nickel.

6. Isomorphism (*q. v.*) is of the greatest importance in the determination of atomic constitution and atomic weights. If in a crystallized compound one substance can be replaced by another *analogous* substance, without alteration of crystalline form, it is to be supposed that this substitution takes place according to equal numbers of atoms. If then there be two compounds of the same crystalline form, and containing in all

respects the same elements, according to the same numbers of atoms, excepting that one contains the substance A, the other the substance B, and there are grounds for supposing that the former contains 1 At. A, or 2 At. A, &c.; then also must it be admitted that the other compound contains 1 At. B, or 2 At. B, &c. There being but one compound of aluminum and oxygen, viz., alumina, this compound might be supposed to contain 1 At. metal + 1 At. oxygen; but alumina crystallizes in sapphire in acute rhombohedrons, just like those of peroxide of iron in specular iron ore and of artificially prepared oxide of chromium. These last mentioned oxides combined with sulphuric acid, potash, and water also form regular octohedrons, just as alumina does in common alum: all these salts contain 4 At. sulphuric acid, 1 At. potash, and 24 At. water. Alumina is then isomorphous with these oxides, and must therefore be made up of the same number of atoms. Since then, according to Principle 4, peroxide of iron is supposed to contain 2 At. metal + 3 At. oxygen, the same must likewise be the case with alumina. Now 100 parts of alumina contain 53·31 aluminum and 46·69 oxygen; and 46·69 : 53·31 = 24 : 27·4; hence with 24 (3 At.) oxygen there are combined 27·4 (2 At.) aluminum; and 1 At. aluminum = 13·7. Again, peroxide of tin in tin-stone crystallizes in the same form as oxide of titanium in rutile; and since, according to Principle 4, it was assumed as probable that peroxide of tin contains 1 At. tin with 2 At. oxygen, this relation must also be supposed to hold good with regard to oxide of titanium. Black oxide of copper forms compounds isomorphous with the analogous compounds of magnesia, oxide of zinc, and protoxide of iron, all of which are supposed to contain 1 At. metal with 1 At. oxygen; such then must also be the case with the black oxide of copper, a conclusion agreeing with that arrived at in 4. Further development of these relations will be found under the head of *Isomorphism*.

For the determination of the atomic weights of simple substances from their specific heats, vid. *Heat*.

The following table of the atomic weights of the elementary bodies is founded almost wholly on the analyses of their compounds performed by Berzelius, a labour as difficult as it was extensive, by which Berzelius has conferred an everlasting obligation on chemical science.

Column A contains the names of the simple substances; B the symbols introduced by Berzelius to denote them; C and D the atomic weights, those, namely, which most probably belong to the several bodies according to the principles just developed; column C, in which the atomic weight of hydrogen = 1 is that which will be used in preference in this work; in D the atomic weight of oxygen = 100. The columns E and F contain the atomic weights according to Berzelius; in E the atomic weight of hydrogen is assumed = 0·5, that of a double atom of hydrogen = 1; in F the atomic weight of oxygen is put = 100. The numbers of this last column are those which are adopted by the majority of chemists after the example of Berzelius. The atomic weights of lanthanum and cerium are given according to the approximate determination of F. J. Otto. (Graham, *Lehrb.* 1, 222.)

Atomic Weights of the Elementary Bodies.

A	B	C	D	E	F
Oxygen	O	8	100	8·01	100·
Hydrogen	H	1	12·5	0·50	6·2398
Carbon	C	6	75	6·13	76·44
Boron	B	10·8	135	10·91	136·20
Phosphorus	P	31·4	392·5	15·72	196·14
Sulphur	S	16	200	16·12	201·17
Selenium	Se	40	500	39·63	494·58
Iodine	I	126	1575	63·28	789·75
Bromine	Br	78·4	980	39·20	489·15
Chlorine	Cl	35·4	442·5	17·74	221·33
Fluorine	F	18·7	233·75	9·37	116·90
Nitrogen	N	14	175	7·09	88·52
Potassium	K	39·2	490	39·26	489·92
Sodium	Na	23·2	290	23·31	290·90
Lithium	L	6·4	80	6·44	80·33
Barium	Ba	68·6	857·5	68·66	856·88
Strontium	Sr	44	550	43·85	547·29
Calcium	Ca	20·5	256·25	20·52	256·02
Magnesium	Mg	12·7	158·75	12·69	158·35
Lanthanum		36·1	451·7		
Cerium	Ce	46·3	578·8		
Didymium					
Yttrium	Y	32·2	402·5	32·25	402·51
Erbium					
Terbium					
Glucinum	G	17·7	221·25	26·54	331·26
Aluminum	Al	13·7	171·25	13·72	171·17
Thorium	Th	59·6	745	59·65	744·90
Zirconium	Zr	22·4	280	33·67	420·20
Silicium	Si	14·8	185	22·22	277·31
Titanium	Ti	24·5	306·25	24·33	303·66
Tantalium	Ta	185	2312·5	92·45	1153·72
Niobium					
Pelopium					
Tungsten	W	95	1187·5	94·80	1183·00
Molybdenum	Mo	48	600	47·96	598·52
Vanadium	V	68·6	857·5	68·66	856·89
Chromium	Cr	28·1	351·25	28·19	351·82
Uranium	U	217	2712·5	217·26	2711·36
Manganese	Mn	27·6	345	27·72	345·89
Arsenic	As	75·2	940	37·67	470·04
Antimony	Sb	129	1612·5	64·62	806·45
Tellurium	Te	64	800	64·25	801·76
Bismuth	Bi	106·4	1330	71·07	886·92
Zinc	Zn	32·2	402·5	32·31	403·23
Cadmium	Cd	55·8	697·5	55·83	696·77
Tin	St	59	737·5	58·92	735·29
Lead	Pb	103·8	1297·5	103·73	1294·50
Iron	Fe	27·2	340	27·18	339·21
Cobalt	Co	29·6	370	29·57	368·99
Nickel	Ni	29·6	370	29·62	369·68
Copper	Cu	31·8	397·5	31·71	395·71
Mercury	Hg	101·4	1267·5	101·43	1265·82
Silver	Ag	108·1	1351·25	108·30	1351·61
Gold	Au	199	2487·5	99·60	1243·01
Platinum	Pt	98·7	1233·75	98·85	1233·50
Palladium	Pd	53·4	667·5	53·36	665·90
Rhodium	R	52·1	651·25	52·2	651·39
Iridium	Ir	98·7	1233·75	98·84	1233·50
Osmium	Os	99·6	1245	99·72	1244·49
Ruthenium	Ru	51·7	646·25		

The discrepancies between the numbers in C D and those in E F are explained by the following considerations. In C D it is supposed that the atomic weight of oxygen is exactly 8 times that of hydrogen, while in E F its value is 8·01 times (or more accurately 8·0083 times) that of the double atom of hydrogen: also in C D the fractions of the other numbers are shortened as much as possible. In E F the atomic weights of hydrogen, iodine, bromine, chlorine, fluorine, and nitrogen are, for reasons above mentioned, reduced one-half. In C D, according to Principle 2, the atomic weights of phosphorus, arsenic, and antimony are doubled; according to C D, the phosphoric, arsenic, and antimonic acids contain 5 At. oxygen for every atom of phosphorus or metal; according to E F these acids contain 2 At. phosphorus or metal for every 5 At. oxygen. In C D it is supposed that glucina and zirconia contain 1 At. glucinum or zirconium with 1 At. oxygen: in E F they contain 2 At. metal to 3 At. oxygen. In C D it is assumed that silica contains 1 At. silicium, combined with 2 At. oxygen: in E F, 1 At. metal with 3 At. oxygen. In C D it is assumed, as was formerly supposed by Berzelius, and is now regarded by him as admissible, that oxide of bismuth contains 3 At. oxygen to every 2 At. metal: in E F it is supposed to contain 1 At. oxygen + 1 At. metal.

On comparing with one another the numbers in column C, we obtain the following results.

1. The atomic weights of the other simple substances are in many instances exact multiples of that of hydrogen, *e. g.*, carbon, oxygen, nitrogen, sulphur, selenium, strontium, molybdenum, &c. Is it then a law of nature, as Prout and Thomson suppose, that the atomic weights of all the elements are divisible by that of hydrogen? If we can entertain the notion that there is but one primary ponderable matter, we must suppose that body to be hydrogen, since hydrogen has the smallest atoms: and it must further be supposed that when these atoms unite in different numbers in such a manner that they are not separable by any method yet discovered, they produce the larger and heavier atoms of the other bodies, whose atomic weights are then necessarily divisible by that of hydrogen. But the atomic weights of most bodies exhibit deviations from this law of such magnitude that Berzelius regards the occasional near divisibility of these weights by that of hydrogen as merely accidental; indeed, according to him, they are never *exactly* divisible, as may be seen by inspection of columns E, F. Nevertheless the later experiments of Dumas and Stass (*Ann. Chim. Phys.* 76, 1), which give the atomic weight of carbon exactly = 6, and those of Liebig and Redtenbacher (*Ann. Pharm.* 38, 113), which make it = 6·088, show that the question is not yet decided.

2. The elements may be arranged in groups, the members of which exhibit similar physical and chemical relations. Whether, as Döbereiner supposes (*Pogg.* 15, 301), such groups necessarily consist of 3 elements arranged in a triad, is a question which we shall not undertake to decide. The atomic weights of such corresponding elements usually bear a simple relation to each other: sometimes they are nearly equal, sometimes exact multiples one of another, or at all events increasing in some simple proportion. The following are similar to one another and have nearly equal atomic weights: chromium 28·1, manganese 27·6, and iron 27·2; cobalt 29·6 and nickel 29·6; zinc 32·2, copper 31·8; platinum 98·7, iridium 98·7, and osmium 99·6. The atomic weights of oxygen, sulphur, selenium, tellurium, and antimony are 8, 16, 40, 64, 129, there-

fore as 1 : 2 : 5 : 8 : 16. The atomic weights of fluorine, chlorine, bromine, and iodine are 18·7, 35·4, 78·4, and 126, which are nearly as 2 : 4 : 9 : 14. Again, half the sum of the atomic weights of chlorine and iodine gives nearly that of bromine, $\frac{35{\cdot}4 + 126}{2} = 80{\cdot}7$, and we find that bromine, in all its physical and chemical relations, holds the middle place between chlorine and iodine. The atomic weights of lithium, sodium, and potassium are 6·4, 23·2, and 39·2; and $\frac{6{\cdot}4 + 39{\cdot}2}{2} = 22{\cdot}8$; the atomic weight of sodium is therefore almost exactly the mean between those of lithium and potassium, just as sodium in other respects holds the middle place between lithium and potassium. The atomic weights of magnesium, calcium, strontium, and barium, are 12·7, 20·5, 44, and 68·6; therefore, nearly as 3 : 5 : 11 : 17: in this instance also by adding the atomic weights of barium and calcium, and dividing by 2, we get nearly the atomic weight of strontium, an element which in all its other relations is intermediate between barium and calcium; $\frac{20{\cdot}5 + 68{\cdot}6}{2} = 44{\cdot}55$. The atomic weight of lanthanum is nearly 3 times that of magnesium. The atomic weights of silicium, zirconium, and thorium are 14·8, 22·4, 59, which = 2 : 3 : 8 nearly. Those of titanium, molybdenum, tungsten, and tantalium are 24·5, 48, 95, 185 = 1 : 2 : 4 : 8 nearly. The atomic weight of manganese is 27·6, of uranium 217, which = 1 : 8 nearly. That of chromium is 28·1, of vanadium 68·6, nearly = 2 : 5. That of phosphorus 31·4 + that of arsenic 75·2 gives 106·6, nearly that of bismuth 106·4. That of palladium is 53·4, of silver 108·1, nearly = 1 : 2. Even if some of these relations should be accidental, and disappear when the atomic weights are determined with greater precision, it may, on the other hand, be expected that the greater number of them will, in such case, come out with mathematical exactness.

Relations between the Atomic Weights of Simple Substances and their Specific Gravities.

The greater the number of atoms of a body in a given space, and the greater the weight of those atoms, the greater must be the specific gravity of the body; hence the specific gravity is the product of the atomic number and the atomic weight; and the specific gravity divided by the atomic weight gives the *Atomic number*, that is to say, *the number of atoms in a given volume*. With bodies which contain equal numbers of atoms in equal volumes, the specific gravity must vary as the atomic weight.

1. *In Elastic Fluids.*

The atomic weight of elastic fluids, whether permanent gases or vapours, bears a simple relation to their specific gravity, that of air = 1, and pressure and temperature being constant. The following table contains in column A the names of certain elements, in B their atomic weights, in C the specific gravities of their gases, in D their atomic numbers obtained by dividing the sp. gr. by the atomic weight; E gives the reduced atomic number obtained on the supposition that 1 volume of hydrogen gas contains 1 atom of hydrogen, the numbers in this column being the quotients obtained by dividing the several numbers in column D

by the atomic number of hydrogen = 0·0693. The last column F gives the specific gravities of the gases, that of hydrogen = 1, by which the simple relation between the specific gravity and the atomic weight becomes still more apparent.

A	B Atomic weight.	C Sp. gr. Air = 1.	D Atomic number.	E Reduced Atomic number.	F Sp. gr. Hydrogen gas = 1.
Sulphur	16	6·9000	0·4312	6	96
Phosphorus.....	31·4	4·4200	0·1408	2	62·8
Arsenic	75·2	10·6000	0·1423	2	150·4
Oxygen	8	1·1093	0·1386	2	16
Hydrogen	1	0·0693	0·0693	1	1
Iodine.....	126	8·7160	0·0691	1	126
Bromine	78·4	5·5400	0·0709	1	78·4
Chlorine	35·4	2·4543	0·0693	1	35·4
Nitrogen	14	0·9706	0·0693	1	14
Mercury	101·4	6·9760	0·0688	1	101·4

According to this table elementary bodies in the gaseous state contain in a given volume either 1 . x or 2 . x or 6 . x atoms. Hence they may be divided into the following classes.

a. Hexatomic gas. Sulphur.

b. Diatomic gases. Phosphorus, arsenic, oxygen.

c. Monatomic gases. Hydrogen, iodine, bromine, chlorine, nitrogen, mercury.

In compound elastic fluids we also meet with $\frac{2}{3}$, $\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$-atomic gases.

When a body assumes the gaseous state, its atoms become surrounded with heat-spheres, whose volumes are as 1 (in the 6-atomic gases); 3 (in the 2-atomic gases); 6 (in the 1-atomic gases); 9 (in the $\frac{2}{3}$-atomic gases); 12 (in the $\frac{1}{2}$-atomic gases); 18 (in the $\frac{1}{3}$-atomic gases); 24 (in the $\frac{1}{4}$-atomic gases. Hence the magnitude of the gas-spheres increases in the simple proportion of 1 : 3 : 6 : 9 : 12 : 18 : 24. The smaller the gas-spheres of any substance, the greater will be the number of them contained in a given space, *e. g.*, of the gas-spheres of sulphur 6 times as many as of the gas-spheres of hydrogen, which are 6 times as large. The cause of the different magnitude of the calorific envelopes in different substances is not known.

The last column of the table, in which the sp. gr. of hydrogen = 1, shows that in all monatomic gases the specific gravity and atomic weight coincide, because the sp. gr. of hydrogen which belongs to this class is assumed = 1; also that the sp. gr. of the 2-atomic gases is twice, and that of the 6-atomic gases 6 times as great as the atomic weight.

In order to bring together two gaseous bodies in equal numbers of atoms, equal volumes of the gases must be taken if the gases belong to the same class; but if one of them contains more atoms than the other in the same volume, then a larger volume of the latter must be taken than of the former; *e. g.*, equal measures of hydrogen and chlorine gases because both are monatomic: on the contrary, 2 measures of hydrogen and 1 of oxygen, because the first is monatomic and the second 2-atomic; similarly, 6 measures of hydrogen gas and 1 of sulphur-vapour, because the former is monatomic and the latter 6-atomic, &c. &c. If it were required

to mix 1 atom of one gas with 2, 3, 4, or a greater number of atoms of the other, or 2 with 3, then in the case of gases of the same class, it would be necessary to mix them in the corresponding proportions by volume of 1 : 2, 3, 4 . . . ., or 2 : 3 as the case might be: if the gases were of different classes, the volume of that gas which contained the smaller number of atoms would require to be multiplied by a corresponding factor. Thus 1 At. sulphur + 2 At. oxygen form sulphurous acid; but since sulphur-vapour contains 3 times as many atoms as oxygen gas, 1 volume of sulphur-vapour will require 3 . 2 = 6 volumes of oxygen gas. It appears from this that all combinations of gaseous bodies take place according to simple proportions by volume; the proportions actually observed are as follows: 1 : 1, 1 : 2, 1 : 3, 1 : 4 (nitrogen and hydrogen in ammonia); 1 : 6, 1 : 9 (sulphur vapour and oxygen gas in sulphuric acid); 2 : 3 (nitrogen and oxygen in nitrous acid); 2 : 5 (nitrogen and oxygen in nitric acid); 2 : 7 (chlorine and oxygen in hyperchloric acid); and 3 : 4 (oxygen and nitric oxide gases to form nitric acid). The cases not here specified will be found in the table, page 67.

Almost all bodies may be brought into the gaseous state by elevation of temperature, and there can be no doubt that those in which this change has not yet been effected, merely require a higher temperature than we have yet been able to produce,—and that these more refractory bodies would, when in the gaseous state, exhibit the same simple relations of specific gravity and atomic weight as the more volatile. Hence we are able to form a probable estimate of the specific gravity which would belong in the gaseous state, even to those bodies which either have not been brought into that state at all, or require so high a temperature to sublime them as to render it impossible to determine the specific gravity of their vapours. For example, carbonic oxide consists of 6 parts (1 At.) of carbon and 8 parts (1 At.) of oxygen; carbonic acid of 6 parts of carbon and 16 parts (2 At.) of oxygen. If now we assume, as is most probable, that carbon vapour like hydrogen gas belongs to the class of monatomic gases, and accordingly that carbonic oxide gas contains 2 measures, and carbonic acid 1 measure of carbon vapour combined with 1 measure of oxygen gas, then the sp. gr. of oxygen gas will be to that of carbon vapour = 16 : 6 = 1·1093 : 0·416; that is to say,—if at a temperature and pressure at which carbon can exist in a state of vapour, 1 vol. of air weighs 1·000, then at the same temperature and pressure, 1 vol. of oxygen gas will weigh 1·1093, and 1 vol. of carbon vapour 0·416. If on the other hand we suppose that carbon vapour is like oxygen, a 2-atomic gas, then carbonic oxide, which contains equal numbers of atoms of the two bodies, must also contain equal volumes, and in carbonic acid there will be 2 vol. of oxygen combined with 1 vol. of carbon vapour; on this hypothesis we have, sp. gr. of oxygen gas : sp. gr. of carbon vapour = 8 : 6 = 1·1093 : 0·832.

2. *In Solids and Liquids.*

In these states of matter, simple relations between specific gravity and atomic weight are for many reasons less frequent.—The larger the atoms of a body, the fewer of them will there be required to fill a given space, unless the intervals are diminished in the same proportion. Difference of cohesion produces different degrees of approximation in the atoms, and thereby causes the magnitude of the intervals to vary. Moreover, the intervals may vary in width in the same substance: thus, a metal cooled after melting is lighter than the same metal after it has

been hammered. Finally, one body expands more by heat than another. All these disturbing causes, which prevent the existence of any exact relation between atomic weight and specific gravity, are absent in gaseous bodies: in these the size of the atoms is so small in comparison with that of the heat-spheres that it need not be taken into consideration; moreover, cohesion is in gases completely overcome, and they all expand equally with equal increments of heat.

The following table is arranged in the same manner as the last.—Column A: the simple substances taken in order according as their atomic numbers for the same volume diminish. Column B: their atomic weights. Column C: their specific gravities in the liquid or solid state, that of water = 1·000; in the case of the metals the sp. gr. are those which they possess after fusion and solidification, not after hammering. Column D: the quotient obtained by dividing the specific gravity by the atomic weight, that is to say, the atomic number. Column E: the quotients in column D multiplied by 770 (air being 770 times lighter than water) in order to render the atomic numbers of this table comparable with those of the former, in which the sp. gr. of air was assumed = 1·000. Column F: the atomic numbers of column E divided by 0·0693; the column F of the present table is thus made to harmonize with column E of the preceding: it gives the number of atoms of a liquid or solid body contained in a space which would include 1 atom of hydrogen. Column G: the numbers taken from column F of the former table, and giving the reduced atomic number of a body in the gaseous state, 1 volume of hydrogen gas being supposed to contain 1 atom of hydrogen.

A	B	C	D	E	F	G
			Atomic Number.			
	Atomic weight.	Specific gravity.	Water = 1.	Air = 1.	Reduced.	In the gaseous state.
Carbon	6	3·5000	0·5833	449·141	6481	1?
Nickel	29·6	8·6370	0·2918	224·686	3242	
Manganese	27·6	8·0000	0·2898	223·146	3220	
Cobalt	29·6	8·5384	0·2885	222·145	3205	
Iron	27.2	7·8439	0·2883	221·991	3203	
Copper	31·8	8·7210	0·2742	211·134	3046	
Platinum	98·7	21·5000	0·2178	167·706	2420	
Titanium	24·5	5·2800	0·2155	165·935	2394	
Palladium	35·4	11·5000	0·2153	165·781	2392	
Rhodium	52·1	11·2000	0·2149	165·473	2388	
Zinc	32·2	6·9154	0·2148	165·396	2386	
Chromium	28·1	5·9000	0·2100	161·700	2333	
Iridium	98·7	18·6300	0·1887	145·299	2096	
Tungsten	95·0	17·4000	0·1831	140·987	2034	
Molybdenum	48	8·6000	0·1792	137·984	1991	
Cadmium	55·8	8·6355	0·1547	119·119	1719	
Mercury	101·4	13·5590	0·1337	102·949	1485	1
Sulphur	16	2·0000	0·1250	96·250	1388	6
Tin	59	7·2900	0·1236	95·172	1373	
Lead	103·8	11·3889	0·1097	84·469	1218	
Selenium	40	4·3100	0·1077	82·929	1196	
Osmium	99·6	10·0000	0·1004	77·308	1116	
Tellurium	64	6·2580	0·0978	75·306	1088	
Silver	108·1	10·4280	0·0964	74·218	1071	
Gold	199	19·2000	0·0961	73·997	1068	

A	B	C	D	E	F	G
			Atomic Number.			
	Atomic weight.	Specific gravity.	Water = 1.	Air = 1.	Reduced.	In the gaseous state.
Bismuth	106·4	9·8220	0·0922	70·994	1024	
Arsenic	75·4	5·9590	0·0792	60·984	880	2
Phosphorus	31·4	1·7500	0·0557	42·889	619	2
Antimony	129	6·7010	0·0519	39·963	576	
Sodium	23·2	0·9722	0·0419	32·263	466	
Uranium	217	9·0000	0·0415	31·955	461	
Iodine	126	4·9480	0·0393	30·261	437	1
Bromine	78·4	2·9800	0·0380	29·260	422	1
Chlorine	35·4	1·3333	0·0376	28·952	418	1
Potassium	39·2	0·8650	0·0221	17·017	245	

By examining this table we arrive at the following results:—

1. Equal volumes of different liquid and solid bodies contain very different numbers of atoms. If 1 cubic inch of hydrogen gas contains 1 . x At. hydrogen, then 1 cub. in. potassium contains 245 . x At. potassium, and 1 cub. in. diamond 6481 . x At. carbon. Of all liquid and solid bodies potassium has the smallest and carbon the greatest (27 times as great) atomic number. This great diversity in the atomic numbers is perhaps to be explained; (*a*) from difference of magnitude in the atoms themselves.—The greater the weight, and therefore also the magnitude of the atoms, the smaller must be the number of them which at equal intervals can be disposed in a given space. This is perhaps one of the causes why uranium which has so large an atomic weight should have so small an atomic number; why sodium, whose atomic weight is not much more than half that of potassium, has an atomic number nearly twice as great. The great atomic number of carbon may likewise partly arise from the smallness of its atoms. (*b.*) From difference in the force of attraction (Cohesion) between the atoms.—The hardest of all substances, the diamond, is precisely that which contains the greatest number of atoms in a given volume: either then its great cohesion is the consequence of the close approximation of its atoms, or this close approximation a consequence of their great cohesion; or possibly, the strong attraction of the particles for one another, together with the close approximation thereby produced, may be the cause of the great tenacity and hardness of the diamond. The other bodies likewise follow nearly in the order of their cohesion, and the soft metal potassium terminates the series. (*c.*) From the different affinities of the atoms for heat.—The stronger this affinity, the greater will be the quantity of heat collected in the pores, and the more widely therefore will the atoms be kept asunder. A greater attraction for heat implies also a greater inclination to assume the gaseous state. Accordingly, the less volatile bodies, those namely which have the smallest attraction for heat, such as carbon and the more refractory metals, exhibit larger atomic numbers than sulphur, selenium, phosphorus, iodine, bromine, chlorine, and the volatile metals. The only exceptions to this rule are zinc and the very refractory metals, uranium, gold, silver, and osmium. In a similar manner, as will afterwards be shown (vid. *Heat*), the specific heat of bodies is greater, *cæteris paribus*, in proportion as they have fewer atoms in a given space and therefore greater

intervals between them. Lastly, the exceptions just noticed and others also show that the three causes here considered, viz., the size of the atoms, their cohesion, and their attraction for heat, are not the only ones by which the atomic numbers are affected.

2. Many elements possessed of similar properties have their atomic numbers nearly equal; *e. g.*, nickel, manganese, cobalt, and iron (of which that of the diamond is double); platinum, palladium, and rhodium; titanium and chromium; tungsten and molybdenum; silver and gold; phosphorus and antimony; iodine, bromine, and chlorine. The atomic numbers of some substances are also simple multiples of others of similar nature; that of copper is nearly double that of mercury: that of zinc double that of lead; of arsenic $1\frac{1}{2}$ times that of antimony; of sodium nearly twice that of potassium.

3. On comparing the atomic numbers of one and the same substance in its gaseous (column G) and in its liquid or solid state (column F), we have the following results:—A space which contains 1 At. chlorine in the gaseous state will hold 418 atoms of liquid chlorine; hence chlorine in passing from the liquid to the gaseous state at a temperature 0° C. and a pressure of 0·76 metres (= 30 inches) is expanded to 418 times its volume. In the case of bromine the expansion amounts to 422 times, of iodine 437, of phosphorus 309, of arsenic 440, of sulphur 231, of mercury 1485, and of carbon (if its vapour be regarded as a monatomic gas) to 6481 times its volume. The great differences between these numbers show the utter groundlessness of the law which Persoz (*Chim. Molec.* 254) thought he had discovered, viz., that all substances both simple and compound, in passing from the gaseous to the liquid or solid state, undergo the same amount of condensation. The specific gravities calculated according to this law appear to coincide with the results of observation, only because Persoz regarded the vapours of sulphur and phosphorus as monatomic gases, and supposed that the sp. gr. of sulphur determined by experiment was not 2 but 1·8, taking also for that of arsenic the totally incorrect number 8·3 determined by Bergman, and long since rectified by Lavoisier, Guibourt, Karsten, and Herapath.

4. Since liquid and solid bodies rarely contain equal numbers of atoms in equal volumes, they exhibit no tendency to combine in those simple proportions by volume which invariably hold good in the combination of gases. If, for example, we would combine 1 cub. in. of sulphur with 1 cub. in. of lead, we should have to bring together $1388 \cdot x$ At. sulphur and $1218 \cdot x$ At. lead, and since these bodies combine in equal numbers of atoms there would remain $170 \cdot x$ At. sulphur uncombined. The differences of the atomic numbers in the table are such that even by multiplying the volume of a body by $1\frac{1}{3}$, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, 4, &c., no exact relations would result. If, moreover, it be considered that the same metal according as its density has or has not been increased by hammering must have a different atomic number, and again that different substances when heated expand in various degrees, so that a proportion by volume correctly determined at one temperature would be incorrect at every other, it will be evident that the endeavours of Meinecke (*Chemische Messkunst*) and of Frère de Montizon (*Ann. Chim. Phys.* 7, 7,) to discover simple relations by volume in the combinations of liquid and solid bodies must necessarily have led to no result whatever.

The so-called Atomic volume. It is inconsistent with the atomic theory to suppose that the space which a body occupies is completely filled by it. For the laws of gravitation oblige us to assign the same specific

gravity to the atoms of different substances, and consequently to suppose that the different weights of these atoms are due to difference of magnitude; *e. g.*, that an atom of double weight must also be of double volume. It follows from this that the specific gravities of different substances must depend upon the magnitude of the spaces existing between their atoms. These atoms must be regarded as impenetrable and of unalterable volume, and the expansion of a body by heat or by diminution of external pressure, as well as its contraction by cooling or increase of pressure, as proceeding from an enlargement or diminution of the intervening spaces. In opposition to this view, which follows almost of necessity from the hypothesis of atoms, Le Royer and Dumas (*J. Phys.* 92, 409) and more lately Graham and Kopp, conceive that the space which a body occupies is completely filled by atoms without any intervening spaces. According to this hypothesis, the specific gravity of a body multiplied by the volume of its atoms, must give the atomic weight (for the greater the sp. gr. of any substance and therefore—according to this view—of its atoms, and the greater their volume, the greater also must be their weight). Conversely, when the atomic weight and specific gravity are known, the *volume of the atoms* will be found by dividing the first by the second. Thus the atomic weight of carbon = 6 divided by the specific gravity of the diamond = 3·5 will give the atomic volume of carbon = 1·714; and the atomic weight of potassium = 39·2 divided by its sp. gr. = 0·865 gives its atomic volume = 45·32. If now these numbers be compared with the atomic numbers of carbon and potassium in column D, it will be found that the so-called atomic volume is exactly the reciprocal of the atomic number; for 1·714 . 0·5833 = 1, and 45·32 . 0·0221 = 1. (It is scarcely necessary to observe that these numbers will come out differently if instead of assuming the atomic weight of hydrogen = 1, we take that of oxygen = 100, as is commonly done). That the atomic volume is necessarily the reciprocal of the atomic number is easily seen: for according to the view first laid down (which must be regarded as the correct one) the specific gravity is the product of the atomic number and the atomic weight (page 52): so that if S = specific gravity, G = atomic weight and Z = atomic number, we have S = G. Z. If now, according to Leroyer, &c., we divide the atomic weight G by the sp. gr. which according to the above is G. Z., we have the atomic volume $= \frac{G}{G.\,Z.} = \frac{1}{Z}$. Hence the atomic volume is the reciprocal of the atomic number. It is easy to see from this that the expression *atomic volume* must lead to erroneous views and inferences: for we can understand by it nothing else than an atom of a body together with the adjacent and surrounding interstices; since, however, these interstices vary according to external circumstances, such as pressure and temperature, the atomic volume must be variable also. This is allowed by Pol. Boullay (*Ann. Chim. Phys.* 43, 266, extr. *Pogg.* 19, 107; also *N. Tr.* 23, 1, 208) who advanced similar views. If this mode of calculation be adopted, it is better to leave the atomic theory out of the question and adopt the nomenclature of H. Schröder, who calls these quotients *equivalent volumes*. Since 16 parts of sulphur are the equivalent of 126 iodine, a volume of sulphur which takes up 16 : 2000 = 8 cubic measures, is the equivalent of 1 vol. iodine which occupies 126 : 4·048 = 25·46 cubic measures; for 1 vol. sulphur of 8 cubic measures, whose sp. gr. = 2 contains 2. 8 = 16 parts by weight, and 1 vol. iodine whose sp. gr. = 4·946 contains 4·946 . 25·46 = 126 parts by

weight. (For further development of this matter, vid. *Density of Compounds.*)

Atomic weight of Compounds.

The two laws above laid down (page 41) apply to compounds as well as to simple substances. If one compound substance A is capable of combining with another compound substance B in different proportions, the smallest quantity of B with which A can combine, multiplied by $1\frac{1}{2}$, 2, 3, 4 . . . . gives the other quantities of B which can enter into combination with A. Thus, 47·2 parts of potash are united in carbonate of potash with 22, and in bicarbonate with 44 parts of carbonic acid:—111·8 oxide of lead can combine with 9, 18, 27 and 54 parts of nitric acid. The second law is also applicable: from the proportions in which one compound substance combines with two others may likewise be determined the proportion according to which these two combine with one another. Hydrate of magnesia contains 20·7 magnesia and 9 water; sulphate of magnesia, 20·7 magnesia and 40 sulphuric acid; and accordingly 9 water and 40 sulphuric acid are exactly the proportions of these two bodies contained in oil of vitriol. In this manner the atomic weights or equivalents of compound bodies may be determined quite independently of those of simple substances. For example, we might assume the atom of sulphuric acid = 1000, and then determine that of water = 225, of magnesia 517·5, and oxide of lead 2795, these being the quantities of these several substances, which combine with 1000 parts of sulphuric acid: moreover, since these quantities of the several bases saturate 1350 nitric acid, this number 1350 would, on the same hypothesis, express the atomic weight of nitric acid. Numbers so determined would not, however, be in accordance with those of the simple substances obtained on the supposition of hydrogen = 1 or oxygen = 100.

The atomic weight of any compound is equal to the sum of the atomic weights of the simple substances which compose it. This is in exact accordance with the atomic theory; for the atom of a compound must weigh as much as the individual atoms of the simple substances composing it taken together. 1 At. hydrogen = 1 and 1 At. oxygen = 8 form 1 At. water = 1 + 8 = 9; 1 At. lead = 103·8 and 1 At. oxygen = 8 form 1 At. oxide of lead = 111·8; 1 At. sulphur = 16 and 3 At. oxygen = 24 form 1 At. sulphuric acid = 16 + 24 = 40. Hence 111·8 parts of oxide of lead combine with exactly 40 parts of sulphuric acid, because this is the proportion in which 1 At. oxide of lead combines with 1 At. sulphuric acid. If 111·8 parts of oxide of lead be heated to redness with an excess of aqueous sulphuric acid, that part of the acid not taken up by the oxide of lead evaporates together with the water, and there remain exactly 151·8 parts of sulphate of lead, containing 111·8 oxide of lead and 40 sulphuric acid. When galena, a compound of 1 At. lead with 1 At. sulphur is digested with nitric acid, which gives to the lead and the sulphur the quantities of oxygen required for converting them respectively into oxide of lead and sulphuric acid, and the liquid is evaporated to dryness, there remains the same compound of 111·8 oxide of lead and 40 sulphuric acid, so that no excess of sulphuric acid can be removed by water or of oxide of lead by acetic acid, because 1 At. lead by combining with oxygen forms exactly 1 At. oxide of lead, and 1 At. sulphur by combining with oxygen forms exactly 1 At. sulphuric acid,—and moreover oxide of lead and sulphuric acid combine precisely in the proportion of 1 atom to 1 atom. It is a necessary concomitant of this law,

gives 4·08 nitrogen; 292 : 20 = 85 : x gives 5·82 hydrogen; and 292 : 48 = 85 : x gives 13·97 oxygen.

The first formula also serves to find how much of any substance, simple or compound, is required to convert a given quantity of another substance into a given compound, or to decompose a given quantity of any compound.—How much sulphur is required to convert 135 parts of copper into disulphuret of copper? In this compound, $Cu^2 S$, there are 2 . 31·8 = 63·6 copper combined with 16 sulphur: since then 63·6 copper require 16 sulphur, 135 parts of copper will require 33·96 parts of sulphur, for 63·6 : 16 = 135 : 33·96.—How much oil of vitriol is required for the decomposition of 79 pts. of nitrate of potash, so that bisulphate of potash may be formed while the nitric acid escapes? In nitrate of potash, 1 At. potash, (KO) = 39·2 + 8 = 47·2 is combined with 1 At. nitric acid (NO^5) = 14 + 40 = 54: the atomic weight of nitrate of potash is therefore 47·2 + 54 = 101·2. Oil of vitriol (SO^3 HO) contains 1 At. sulphuric acid = 16 + 3 . 8 = 40, and 1 At. water = 1 + 8 = 9: therefore the atomic weight of oil of vitriol is 40 + 9 = 49. Since then 2 At. sulphuric acid are to combine with 1 At. potash, 1 At. or 101·2 parts of nitrate of potash (containing 47·2 potash) will require 2 At. or 2 . 49 = 98 parts of oil of vitriol (containing 80 sulphuric acid); now 101·2 : 98 = 79 : 76·5 the quantity of oil of vitriol required to decompose 79 parts of nitrate of potash.

By means of the second formula we may find the atomic weight of a substance when we know the relative quantity of it in a given compound, and also the number of its atoms which probably enter into the constitution of that compound. Suppose that in 100 parts of selenious acid we have found 71·43 parts of selenium and 28·57 parts of oxygen, and assume as probable that it contains 1 At. selenium and 2 At. oxygen; we have then, in order to perform the operation indicated by the second formula, to divide the quantity of each element by the number of its atoms: thus

	M	: Z =	G
Se	71·43	: 1 =	71·43
O	28·57	: 2 =	14·285

According to this, the atomic weight of selenium would be 71·43 if that of oxygen were 14·285; but taking 8 for the atomic weight of oxygen, we have 14·285 : 71·43 = 8 : 40: if the atomic weight of oxygen be 100 we have 14·285 : 71·43 = 100 : 500. Hence the atomic weight of selenium is 40 when that of oxygen is 8, and 500 when that of oxygen is 100.

By the third formula we find in what numbers the atoms of the different constituents are united, when their relative quantities and atomic weights are known. If 100 parts of nitric acid contain 25·926 nitrogen, and 74·074 oxygen, and the atomic weights of nitrogen and oxygen are 14 and 8 respectively, what are the numbers of atoms of these two elements contained in nitric acid? According to the formula, the relative quantity divided by the atomic weight gives the number of atoms; therefore

	M	: G =	Z
N	25·926	: 14 =	1·852
O	74·074	: 8 =	9·260

According to this, 1852 At. nitrogen are united with 9260 At. oxygen. This complicated ratio may however (as in most other cases) be

reduced by assuming the atomic number of the elements which gives the smallest quotient in the calculation = 1, and dividing the other quotients by this smallest quotient. Thus in the present example 1·852 : 9·260 = 1 : 5; consequently 1 At. nitrogen is combined with 5 At. oxygen.

Felspar contains in 100 parts, 16·65 potash, 18·14 alumina, and 65·21 silica: how many atoms of these three substances does it contain? Here we have to calculate the atomic weights of the three proximate elements: thus

K 39·2	2Al 27·4	Si 14·8
O 8·	3O 24	2O 16
Potash 47·2	Alumina 51·4	Silica 30·8

	M : G = Z
Potash.....	16·65 : 47·2 = 0·3528
Alumina.....	18·14 : 51·4 = 0·3528
Silica.....	65·21 : 30·8 = 2·1172

Now 3528 : 3528 : 21172 = 1 : 1 : 6. Consequently felspar contains 1 At. potash, 1 At. alumina, and 6 At. silica, probably combined as follows:

$$(KO, 3SiO^2) + (Al^2O^3\ 3SiO^2).$$

In many compounds, especially of the organic class, all the elements occur in more than 1 atom, and the division of the larger quotients by the smallest gives improper fractions, which must be got rid of by supposing the number of atoms of the element which gives the smallest quotient to be 2, 3, 4, &c. Dry benzoic acid, for example, contains in 100 parts, 74·34 carbon, 4·42 hydrogen, and 21·24 oxygen.

	M : G = Z
C	74·336 : 6 = 12·390
H	4·425 : 1 = 4·425
O	21·239 : 8 = 2·655

2·655 : 4·425 : 12·390 = 1 : 1·66 .... : 4·66 ...., or multiplying by 3, = 3 : 5 : 14. Hence dry benzoic acid contains 3 At. oxygen, 5 At. hydrogen, and 14 At. carbon.

To save the trouble of making such calculations by the rule of three, Wollaston (*Ann. Phil.* 4, 176; comp. also *Schw.* 14, 126) introduced his *Scale of Chemical Equivalents* constructed on the principle of the ordinary *Sliding Rule*. A slide moveable up and down the middle of a narrow board is marked with the numbers 10 .... 500 placed at distances corresponding to their logarithms, so that, for example, the distance between 10 and 11 is as great as that between 100 and 110. On the right and left of the slide the names of the elementary substances and their more important compounds are marked on the board in places corresponding to their atomic weights. When the slide is set right in the board, that is to say, not drawn either up or down—the number 10 on the slide stands opposite 1 At. oxygen on the board; 11·25 on the slide opposite to 1 At. water on the board; so likewise 12·5 corresponds to 10 At. hydrogen; 20 to 2 At. oxygen, and 1 At. sulphur; 30 to 3 At. oxygen; 40 to 4 At. oxygen; 50 to 5 At. oxygen and 1 At. sulphuric acid; 130 to lead; 140 to oxide of lead; 190 to sulphate of lead, and so on. Consequently, in this position of the slide it may be seen that 190 parts of sulphate of lead contain 140 oxide of lead and 50 sulphuric acid; or 130 lead, 20 sulphur and 40 oxygen, it being supposed that the numbers of atoms of the con-

stituents are previously known. If now it be required to find what quantities of these several elements are contained in 100 parts of sulphate of lead, the slide is to be so placed that the number 100 shall stand exactly opposite to sulphate of lead, when the required quantities will be found opposite the names of the several elements. In this and other ways the Equivalent-scale (which may also be made with a moveable circle instead of a slide) may be employed. However, the fractional parts of the numbers cannot be marked on the divisions of the slide with a degree of accuracy equal to that which may be obtained by calculation, and moreover the number of the elements and their compounds is so great that their names cannot all be marked on the board, so that searching for them in this manner often takes a longer time than calculation: hence the use of these Equivalent-scales has not become very general.

D. Qualitative alterations of elements caused by chemical combination.

Since the chemical combination of heterogeneous substances produces a homogeneous mass, it must necessarily be accompanied by a change in the properties of the elements. In the less intimate combinations this change is very unimportant, no more in many cases than is necessary to cause the different properties of the elements to merge into one another. Thus common salt when dissolved in water loses its solid form and imparts its saline taste to the water, while the specific gravity of the solution is nearly a mean between that of the salt and that of the water. The properties of the more intimate compounds on the other hand are in almost all cases totally different from those of their elements. The two tasteless substances oxygen and sulphur produce by combination the intensely sour and corrosive sulphuric acid; the solid substances carbon and sulphur form when combined the volatile sulphuret of carbon: grey mercury and yellow sulphur form the bright red compound vermillion; &c. &c. Although all the elements of a compound body exert some influence in determining its properties, this influence is nevertheless exerted in very different degrees; it often happens that one element is much more effective in determining the physical and chemical characters of a compound than another; the former may be said to possess more *formative power*, while the latter serves either as a *base* or *groundwork*. Thus the metals may be said to act as bases, while the non-metallic elements, particularly oxygen, hydrogen, chlorine, fluorine, bromine, iodine, selenium and sulphur may be regarded rather as formative principles. The former, when they possess considerable specific gravity, impart this property more especially to the compounds, while the latter generally destroy the metallic lustre, opacity, and great conductive power of heat and electricity by which metals are distinguished, and impart to the compounds peculiar chemical characters, *e. g.*, those of acids or salifiable bases. There is more resemblance between the compounds of oxygen with different metals, as also between the several metallic chlorides, sulphurets, &c. than between the compounds of one and the same metal with oxygen, chlorine, sulphur, &c.

a. Density.

In most instances, the compound occupies a smaller space than its elements taken together before combination; condensation generally takes place, less frequently expansion, or neither.

a. Relation between the Density of Gaseous Compounds and that of their Gaseous Elements.

Most combinations of this class are attended with condensation, and always according to simple relations of volume; many however take place without alteration of bulk so that the compound takes up the same space as the sum of the elements before combination: we know of but one combination of gases which is accompanied by expansion.

These relations are exhibited in the following table. The first division includes the cases in which no change of volume takes place; the second those attended with condensation; the third the single case accompanied by expansion. But few organic compounds are mentioned in this table, as their relations of volume will be fully treated of in another place.

Column A. Names of the compounds.

B. Their chemical formulæ.

C. The number of measures in which the bodies combine.

D. The sum of these measures or the volume of the elements before combination.

E. The number of measures occupied by these elements after combination.

F. The atomic weight of the compound.

G. Spec. grav. of the compound, that of air being assumed = 1.

H. Quotient obtained by dividing the sp. gr. by the atomic weight, *i.e.* the atomic number.

I. Reduced atomic number, obtained on the supposition that 1 vol. hydrogen gas contains 1 . x atoms of hydrogen.

The columns F, G, H, I are comparable with columns B, C, D, E of the table, page 55.

Since the specific gravities of many simple substances occurring in the compounds here enumerated is not known from observation, we are obliged in regard to them to calculate the sp. gr. and thence the relation by volume hypothetically. Thus from analogy, the vapours of selenium and tellurium have been assumed to be 6-atomic, that of antimony 2-atomic, and fluorine gas together with the vapours of carbon, boron, silicium, titanium, tin and bismuth as 1-atomic. Since for example the atomic weight of tin is 59 times as great as that of hydrogen, and the sp. gr. of hydrogen gas = 0·0693, the hypothetical sp. gr. of vapour of tin = 59 . 0·0693. The atomic weight of antimony is 1·29, and its vapour is supposed to be 2-atomic, hence the hypothetical sp. gr. of its vapour is 2 . 129 . 0·0693; to find that of selenium we multiply by 6 . 40, and so on. The hypothetical parts of the calculation are denoted in the table by notes of interrogation: in most cases the hypothetical element is the number of volumes; in that of nitric acid it is the sp. gr of the vapour

A	B Formula.	C Volumes.	D	E	F At. weight	G Spec. grav.	H Atomic number.	I Equivalent
Hydriodic acid	I H	1I, 1H	2	2	127	4·3677	0·0344	1
Hydrobromic acid	Br H	1Br, 1H	2	2	79·4	2·7512	0·0347	1
Hydrochloric acid	Cl H	1Cl, 1H	2	2	36·4	1·2618	0·0347	1
Hydrocyanic acid	Cy H	1Cy, 1H	2	2	27	0·9359	0·0346	1
Bromide of cyanogen	Cy Br	1Cy, 1Br	2	2	104·4	3·6070	0·0345	1
Volatile chloride of cyanogen	Cy Cl	1Cy, 1Cl	2	2	61·4	2·1285	0·0346	1
Nitric oxide	N O^2	1N, 1O	2	2	30	1·0399	0·0346	1
Hydriod. phosph. hydrogen	P H^3, I H	1P H^2, 1I H	2	2	161·4	2·7690	0·0172	1
Hydrobrom. phosph. hydrogen	P H^3, Br H	1P H^3, 1Br H	2	2	113·8	1·9060	0·0168	1
Hydrochlorate of ammonia	N H^3, Cl H	1N H^3, 1Cl H	2	2	53·4	0·8900	0·0167	1
Hydrocyanate of ammonia	N H^3, Cy H	1N H^3, 1Cy H	2	2	44	0·7700	0·0175	1
Bihydrosulph. ammonia	N H^3, 2S H	1N H^3, 1S H	2	2	51	0·8840	0·0173	1
Carbonate of ammonia	N H^3, C O^2	2N H^3, 1CO^2	2	2	39	0·9000	0·0231	1
Sulphurous acid	S O^2	1S, 6O	7	6	32	2·2186	0·0693	1
Selenious acid	Se O^2	1?Se, 6O	7	6	56	4·0000	0·0714	1
Sulphuretted hydrogen	S H	1S, 6H	7	6	17	1·1786	0·0693	1
Seleniuretted hydrogen	Se H	1?Se, 6H	7	6	41	2·7950	0·0681	1
Telluretted hydrogen	Te H	1?Te, 6H	7	6	65	4·4900	0·0691	1
Sulphuret of carbon	C S^2	3?C, 1S	4	3	38	2·6345	0·0693	1
Phosphuretted hydrogen	P H^3	1P, 6H	7	4	34·4	1·1910	0·0346	½
Arseniuretted hydrogen	As H^3	1As, 6H	7	4	78·2	2·6950	0·0345	½
Terchloride of phosphorus	P Cl^3	1P, 6Cl	7	4	137·6	4·8765	0·0355	½
Iodide of arsenic	As I^3	1As, 6I	7	4	453·2	16·1000	0·0355	½
Chloride of arsenic	As Cl^3	1As, 6Cl	7	4	181·4	6·3006	0·0347	½
Terchloride of antimony	Sb Cl^3	1?Sb, 6Cl	7	4	235·2	7·8000	0·0331	½
Water	H O	2H, 1O	3	2	9	0·6239	0·0693	1
Carbonic oxide	C O	2?C, 1O	3	2	14	0·9709	0·0693	1
Nitrous oxide	N O	2N, 1O	3	2	22	1·5252	0·0693	1
Hyponitric acid	N O^4	1N, 2O	3	2	46	1·7200	0·0373	½
Oxide of chlorine	Cl O^4	1Cl, 2O	3	2	67·4	2·3365	0·0347	½
Sub-bromide of mercury	Hg^2 Br	2Hg, 1Br	3	2	281·2	10·1410	0·0360	½
Sub-chloride of mercury	Hg^2 Cl	2Hg, 1Cl	3	2	238·2	8·3500	0·0350	½
Sulphuric acid	S O^3	1S, 9O	10	6	40	3·0000	0·0750	1
Perchloride of phosphorus	P Cl^5	1P, 10Cl	11	6	208·4	4·8500	0·0233	⅓
Ammonia	N H^3	1N, 3H	4	2	17	0·5893	0·0346	½
Chloride of boron	B Cl^3	1?B, 3Cl	4	2	116·7	3·9420	0·0338	½
Fluoride of boron	B F^3	1?B, 3?F	4	2	66·6	2·3124	0·0347	½
Carbonic acid	C O^2	1?C, 1O	2	1	22	1·5252	0·0693	1
Phosgene gas	C O, Cl	1C O, 1Cl	2	1	49·4	3·4249	0·0693	1
Chloro-sulphuric acid	S O^2, Cl	1S O^2, 1Cl	2	1	67·4	4·6650	0·0693	1
Iodide of mercury	Hg I	1Hg, 1I	2	1	227·4	15·9000	0·0699	1
Bromide of mercury	Hg Br	1Hg, 1Br	2	1	179·8	12·1600	0·0676	1
Chloride of mercury	Hg Cl	1Hg, 1Cl	2	1	136·8	9·8000	0·0716	1
Chloride of bismuth	Bi^2 Cl^3	2?Bi, 3Cl	5	2	313	11·3500	0·0356	⅖
Cyanogen	N C^2	1N, 2?C	3	1	26	1·8026	0·0693	1
Chloride of silicium	Si Cl^2	1?Si, 2Cl	3	1	85·6	5·9390	0·0693	1
Fluoride of silicium	Si F^2	1?Si, 2?F	3	1	52·2	3·6050	0·0690	1
Chloride of titanium	Ti Cl^2	1?Ti, 2Cl	3	1	95·3	6·8360	0·0716	1
Bichloride of tin	Sn Cl^2	1?Sn, 2Cl	3	1	129·8	9·1997	0·0708	1
Light carburetted hydrogen	C^2 H^4	2?C, 4H	6	2	16	0·5546	0·0347	½
Solid chloride of cyanogen	Cy^2 Cl^3	3Cy, 3Cl	6	2	184·2	6·3900	0·0347	½
Nitric acid	N O^5	2N, 5O	7	2	54	?3·7422	0·0693	1
Arsenious acid	As O^3	1As, 3O	4	1	99·2	13·8500	0.1396	2
Dichloride of sulphur	S^2 Cl	1S, 3Cl	4	1	67·4	4·7000	0·0696	1
Olefiant gas	C^4 H^4	4?C, 4H	8	2	28	0·9706	0·0347	½
Glacial acetic acid	C^4 H^4 O^4				60	2·7400	0·0457	⅓
Sulphuret of mercury	Hg S	6Hg, 1S	7	9	117·4	5·5100	0·0469	⅔

From this table the following results may be deduced:—

1. Compound bodies in the gaseous state are more expanded, and contain fewer atoms in a given volume than simple substances in the same state. While the simple gases are 6, 2, and 1-atomic, the compound gases are never 6-atomic, but

a. 2-atomic; arsenious acid;

b. 1-atomic; water, nitrous oxide, most oxygen acids, the weaker hydrogen acids, such as sulphuretted hydrogen and several metallic iodides, bromides and chlorides, some containing one and some two atoms of the salt-radical;

c. $\frac{2}{3}$-atomic, sulphuret of mercury and glacial acetic acid;

d. $\frac{1}{2}$-atomic: oxide of chlorine, hyponitric acid, the stronger hydracids, such as hydrochloric acid, ammonia, compounds of 3 At. hydrogen, iodine, bromine or chlorine with 1 At. boron, phosphorus or metals, and those of 1 At. bromine or chlorine with 2 At. mercury;

e. $\frac{1}{3}$-atomic; anhydrous carbonate of ammonia (NH^3, CO^2), perchloride of phosphorus;

f. $\frac{1}{4}$-atomic; compounds of hydracids with ammonia and with phosphuretted hydrogen.

It is scarcely necessary to remark that by $\frac{2}{3}$, $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}$-atomic gases, we are not to understand gases really containing two-thirds, one-half, one-third or one-fourth parts of atoms, but gases of which 1 volume contains only $\frac{2}{3}$, $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}$ as many atoms as an equal volume of hydrogen gas. It appears as if the greater number of atoms, which together form a compound atom, attach to themselves a greater quantity of heat, so that the compound atom becomes surrounded with a larger calorific envelope.

2. The volume of the constituents bears to that of the compound the following relations:—

1 vol. A with 1 vol. B forms 2 vol. AB, therefore $1 + 1 : 2 = 2 : 2$. To this case belong the first 12 examples in the table.

$1 + 1 : 1 = 2 : 1$, Carbonic acid, phosgene, iodide, bromide, and chloride of mercury.

$1 + 2 : 3 = 3 : 3$, Neutral carbonate of ammonia.

$1 + 2 : 2 = 3 : 2$, Water and the 6 following compounds.

$1 + 2 : 1 = 3 : 1$, Cyanogen and the 4 following compounds, supposing the hypothetical relations of volume to be correct.

$1 + 3 : 3 = 4 : 3$, Sulphuret of carbon, with the same limitation.

$1 + 3 : 2 = 4 : 2$, Ammonia, with the 2 following hypothetical cases.

$1 + 3 : 1 = 4 : 1$, Dichloride of sulphur, arsenious acid.

$1 + 6 : 9 = 7 : 9$, Sulphuret of mercury.

$1 + 6 : 6 = 7 : 6$, Sulphurous acid and the 4 following compounds.

$1 + 6 : 4 = 7 : 4$, Phosphuretted hydrogen and the 5 following compounds.

$1 + 9 : 6 = 10 : 6$, Sulphuric acid.

$1 + 10 : 6 = 11 : 6$, Perchloride of phosphorus.

$2 + 3 : 2 = 5 : 2$, Chloride of bismuth?

$2 + 5 : 2 = 7 : 2$, Nitric acid?

$3 + 3 : 2 = 6 : 2$, Solid chloride of cyanogen.

β. *Relations between the Density of Solid or Liquid Compounds, and that of their Solid or Liquid Constituents.*

There is no known instance in which the combination of solid or

liquid bodies takes place without alteration of volume. In most cases condensation ensues, very rarely expansion; a very slight expansion takes place in the combination of iodine with potassium, lead, mercury, or silver, of sulphur with arsenic (in the formation of the red sulphuret) with copper (in the formation of disulphuret of copper) or with cadmium, (Karsten, Boullay,) and of lead with tin, gold, or platinum (Kupffer); also a considerable expansion in the combination of carbon (of 3·5 sp. gr.) with sulphur (of 2·0 sp. gr.) to form bisulphuret of carbon (of 1·272 sp. gr.). But these expansions or contractions exhibit, as might be expected from the reasons stated on page 54, no such simple relation as that which is observed in all cases of the combination of gases. That some approach to a definite relation does however exist between the density of elements and that of their combinations in the solid or liquid state, appears from the labours of Le Royer and Dumas, Herapath (*Phil. Mag.* 1824, *Nov.* 321; abstr. *N. Tr.* 11, 164), Pol. Boullay (*Ann. Chim. Phys.* 43, 266, also *Pogg.* 19, 107, also *N. Tr.* 23, 1, 208), Karsten, Ammermüller, H. Kopp, and especially of H. Schröder.

These relations are exhibited in the following table, which, however, is drawn up, not according to the Theory of Volumes of Kopp and Schröder, but according to the Atomic Theory.

Column A. Name of compound.—B. Formula.

C. Atomic weight.—D. Specific gravity in the liquid or solid state, that of water = 1.

E. Name of the observer of the specific gravity. Bg. denotes Bergman; Bk. Brooke; Bl. Boullay; Bt. Breithaupt; Bu. Bucholz; By. Bussy; Bz. Berzelius; Dm. Dumas; Dt. Dalton; Dv. Davy; Ek. Eckeberg; Fd. Faraday; Gb. Guibourt; GL. Gay-Lussac; Gk. Glocker; Hd. Haidinger; Hf. Hoffmann; Hr. Herapath; Ke. Kersten; Kf. Kupffer; Kn. Karsten; Kp. Kopp; Kw. Kirwan; Ld. Leonhard; Ms. Mohs; Mt. Mitscherlich; Ne. Neumann; Ni. Niemann; Ph. Phillips; RD. Le Royer and Dumas; Rm. Rammelsberg; Rt. Regnault; St. Stromeyer; Ta. Taylor; Te. Thénard; Ti. Thilorier; To. Thomson; Un. Unverdorben; Ur. Ure; W. Wöhler.

F. Quotient obtained by dividing the sp. gr. by the atomic weight; this column is therefore comparable with column D of table, page 55.

G. Numbers in column F multiplied by 770 and then divided by 0·0693 for reasons explained on page 55. Hence the numbers in column G show the number of atoms of a compound included in the space which would contain one atom of hydrogen in the state of gas. Thus then the numbers in column G are comparable with those of column E of table, page 53, as well as those in column F of table, p. 55, and those of column I of table, page 66. For explanation of columns H and I see page 75.

A	B	C Atom. Weight.	D Spec. Grav.	E	F Atom. Number.	G	H	I
Suboxide of copper.....	Cu^2O	71·6	5·300	Bl	0·0740	822	2, 2	883
			5·751	Kn	0·0803	892		
			6·093	Hr	0·0851	945		
Suboxide of mercury....	Hg^2O	210·8	8·950	Kn	0·0425	472	6, 1	475
			10·690	Hr	0·0507	563		
Water	HO	9	1·000	Kn	0·1111	1234	1, 1	1234
Potash.....	KO	47·2	2·656		0·0563	625	1, $\frac{1}{2}$	625
Soda.....	NaO	31·2	2·805	Kn	0·0899	999	1, $\frac{1}{2}$	1048
Baryta.....	BaO	76·6	4·732	Kn	0·0618	687		

A	B	C Atom. Weight.	D	E	F	G	H	I
			Spec. Grav.		Atom. Number.			
Strontia	Sr O	52	3·932	Kn	0·0756	840		
Lime	Ca O	28·5	3·161	Kn	0·1109	1232		
			3·179	Bl	0·1115	1239		
Magnesia	Mg O	20·7	3·200	Kn	0·1546	1718		
Yttria	Y O	40·2	4·842	Ek	0·1177	1308		
Glucina	G O	25·7	2·967	Ek	0·1155	1283		
Thorina	Th O	67·6	9·402	Bz	0·1406	1562		
Protoxide of uranium	U O	225	7·193	Kn	0·0319	354	3, 1	347
Protoxide of manganese	Mn O	35·6	4·726	Hr	0·1327	1474	2, 1	1497
Oxide of zinc	Zn O	40·2	5·600	Bl	0·1393	1548	1, 1	1522
			5·734	Kn	0·1426	1584		
Oxide of cadmium	Cd O	63·8	6·950	Kn	0·1089	1210	1, 1	1220
Protoxide of tin	Sn O	67	6·639	Hr	0·0991	1101	1, 1	1034
Protoxide of lead	Pb O	111·8	9·209	Kn	0·0823	944	1, 1	944
			9·277	Hr	0·0829	921		
			9·600	Bl	6·0849	943		
Oxide of copper	Cu O	39·8	6·401	Hr	0·1608	1787	1, 1	1763
			6·430	Kn	0·1616	1795		
Red oxide of mercury	Hg O	109·4	11·000	Bl	0·1005	1117	½, 1	1148
			11·191	Kn	0·1023	1137		
			11·290	R D	0·1032	1147		
Oxide of silver	Ag O	116·1	7·143	Hr	0·0615	683	2, 1	709
			7·250	Bl	0·0624	693		
			8·256	Kn	0·0711	790		
Red oxide of manganese	$Mn^3 O^4$	114·8	4·722	Hd	0·0411	457	4, 4	455
Red lead	$Pb^3 O^4$	343·4	8·620	Kn	0·0251	279	1, 4	282
			9·082	Hr	0·0264	293		
Magnetic oxide of iron	$Fe^3 O^4$	113·6	5·094	Ms	0·0448	498	3, 4	509
—— artificial			5·400	Bl	0·0475	528		
Alumina, corundum	$Al^2 O^3$	51·4	3·909	Ms	0·0780	867		
—— ruby			3·531	Br	0·0687	763		
Oxide of chromium	$Cr^2 O^3$	80·2	5·210	Wl	0·0650	722	2, 2	749
Oxide of bismuth	$Bi^2 O^3$	236·8	8·173	Kn	0·0345	383	2, 2	411
			8·449	R D	0·0357	396		
			8·968	Bl	0·0379	421		
Peroxide of iron, specular iron ore	$Fe^2 O^3$	78·4	5·251	Ms	0·0669	743	3, 2	744
Oxide of cobalt	$Co^2 O^3$	83·2	5·600	Bl	0·0673	748	3, 2	742
Peroxide of nickel	$Ni^2 O^3$	83·2	4·846	Hr	0·0583	648	3, 2	742
Peroxide of hydrogen	$H O^2$	17	1·452	Te	0·0854	949	2, 1	354
Carbonic acid	$C O^2$	22	0·830	Ti	0·0377	419	6, 6	424
Sulphurous acid	$S O^2$	32	1·420	Fd	0·0444	493	¼, 2	501
			1·450	By	0·0453	503		
Silica	$Si O^2$	30·8	2·652	R D	0·0861	957		
Oxide of titanium, anatase	$Ti O^2$	40·5	3·826	Ms	0·0945	1050	2, 1	1119
—— rutile			4·249	Ms	0·1049	1165		
—— artificial			3·931	Kn	0·0971	1079		
Oxide of tungsten	$W O^2$	111	12·111	Kn	0·1091	1212	½, 2	1178
Oxide of molybdenum	$Mo O^2$	64	5·606	Bz	0·0876	973	2, 1	1022
Peroxide of manganese	$Mn O^2$	43·6	4·940	Hd	0·1133	1259	2, 1	1271
Peroxide of tin, tinstone	$Sn O^2$	75	6·960	Ms	0·0928	1031	1, 1	1034
—— artificial			6·900	Bl	0·0920	1022		
—— artificial			6·639	Hr	0·0885	983		
Peroxide of lead	$Pb O^2$	119·8	8·903	Hr	0·0743	825	½, 1	848
			8·933	Kn	0·0745	828		
			9·190	Bl	0·0767	852		
Boracic acid	$B O^3$	43·8	1·830	R D	0·0526	584	⅔, 1	848
Sulphuric acid	$S O^3$	40	1·970	By	0·0492	547	½, 2	544
Tantalic acid	$Ta O^3$	209	6·500	Ek	0·0311	345		
Tungstic acid	$W O^3$	119	5·274	Hr	0·0443	492	2, 2	685
			6·120	Bz	0·0514	571		
			7·140	Kn	0·0600	667		
Molybdic acid	$Mo O^3$	72	3·460	Bg	0·0486	540	⅔, ⅔	540
Arsenious acid, vitreous	$As O^3$	99·2	3·698	R D	0·0372	413	5, 1	429
			3·703	Kn	0·0373	414		
			3·739	Gb	0·0377	419		

A	B	C Atom. Weight.	D	E	F	G	H	I
			Spec. Grav.		Atom. Number.			
Arsenious acid, vitreous	AsO^3	99·2	3·798	Ta	0·0383	425		
—— — opaque			3·695	Gb	0·0363	403	6, 1	403
Oxide of antimony, natural	SbO^3	153	5·560	Ms	0·0363	403	3, 1	408
—— artificial			5·778	Bl	0·0378	420		
Oxide of chlorine	ClO^4	67·4	1·500	Ni	0·0222	247	7, 1	248
Hyponitric acid	NO^4	46	1·451	G L	0·0315	350		
Antimonious acid	SbO^4	161	6·525	By	0·0405	450	2, 1	450
			6·695	Kn	0·0416	462		
Arsenic acid	AsO^5	115·2	3·734	Kn	0·0324	360	2, 2	364
Antimonic acid	SbO^5	169	6·525	Bl	0·0386	429	$\frac{2}{3}$, 1	429
Spinell	MgO, Al^2O^3	72·1	3·550	Bt	0·0492	547	1, 1	528
Ilmenite	FeO, TiO^2	75·7	4·760	Kf	0·0629	699		
Carbonate of potash	KO, CO^2	69·2	2·264	Kn	0·0327	363	$\frac{1}{2}$, 1	357
—— soda	NaO, CO^2	53·2	2·466	Kn	0·0463	514	$\frac{1}{2}$, 1	513
—— silver	AgO, CO^2	138·1	6·070	Kn	0·0440	489		
—— lime, calcspar	CuO, CO^2	50·5	2·721	Ms	0·0539	599	$\frac{1}{3}$, $\frac{1}{3}$	595
			2·750	Ne	0·0544	604		
—— magnesia	MgO, CO^2	42·7	3·056	Ms	0·0715	794	$\frac{1}{4}$, $\frac{1}{4}$	793
Bitterspar	$CaO, MgO, 2CO^2$	93·2	2·884	Ms	0·0309	343		
Carbonate of manganese (nat.)	MnO, CO^2	57·6	3·550	Ms	0·0616	684		
			3·592	Ms	0·0624	693		
Carbonate of zinc (nat.)	ZnO, CO^2	62·2	4·376	Kn	0·0703	781	$\frac{1}{4}$, 1	804
			4·442	Ms	0·0714	793		
Carbonate of cadmium	CdO, CO^2	85·8	4·494	Kn	0·0523	581		
Spathic iron	FeO, CO^2	57·2	3·872	Ne	0·0676	751		
Mesitin-spar	$MgO, FeO, 2CO^2$	99·9	3·356	Ms	0·0335	372		
Arragonite	CaO, CO^2	50·5	2·931	Ms	0·0580	644		
Witherite	BaO, CO^2	98·6	4·302	Kn	0·0436	484	$\frac{1}{3}$, $\frac{1}{3}$	490
Strontianite	SrO, CO^2	74	3·624	Kn	0·0489	543	$\frac{1}{3}$, $\frac{1}{3}$	559
Carbonate of lead (nat)	PbO, CO^2	133·8	6·428	Kn	0·0480	533		
Junkerite	FeO, CO^2	57 2	3·818	Ms	0·0666	740		
Boracite	$3MgO, 4BO^3$	201·3	2·955	Rm	0·0147	163		
Sulphate of potash	KO, SO^3	87·2	2·623	Kn	0·0301	334	1, $\frac{1}{3}$	345
			2·662	Kp	0·0305	339		
Sulphate of soda	NaO, SO^3	71·2	2·631	Kn	0·0369	410	1, $\frac{1}{3}$	401
			2·462	Kp	0·0346	384		
Sulphate of silver	AgO, SO^3	156·1	5·341	Kn	0·0342	380	1, $\frac{1}{3}$	374
—— zinc	ZnO, SO^3	80·2	3·400	Kn	0·0424	471	1, $\frac{1}{3}$	463
—— copper	CuO, SO^3	79·8	3·572	Kn	0·0448	498	1, $\frac{1}{3}$	497
—— magnesia	MgO, SO^3	60·7	2·607	Kn	0·0429	477	1, $\frac{1}{3}$	473
—— lime	CaO, SO^3	68·5	2·927	Kn	0·0427	474	1, $\frac{1}{3}$	476
			2·960	R D	0·0432	480		
Sulphate of strontia, artif.	SrO, SO^3	92	3·588	Kn	0 0390	433	1, $\frac{1}{4}$	449
—— cœlestin			3·958	Ne	0·0430	478		
Heavy spar	BaO, SO^3	116·6	4·200	Kn	0·0360	400	1, $\frac{1}{3}$	432
			4·446	Ms	0·0381	423		
Sulphate of lead	PbO, SO^3	151·8	6·169	Kn	0·0406	451	1, $\frac{1}{3}$	458
			6·298	Ne	0·0414	460		
Chromate of potash	KO, CrO^3	99·3	2·640	Kn	0·0266	295		
—— lead	PbO, CrO^3	163·9	6·004	Ms	0·0366	407		
Bichromate of potash	$KO, 2CrO^3$	151·4	2·603	Kn	0·0172	161		
Tungstate of lime	CaO, WO^3	147·5	6·040	Kn	0·0409	454	1, 1	433
—— lead	PbO, WO^3	230·8	8·000	Ld	0·0346	384	1, 1	391
Molybdate of lead	PbO, MoO^3	183·8	6·760	Ms	0·0367	408	1, $\frac{1}{3}$	419
Nitrate of ammonia	NH_4O, NO^5	80	1·707	Kp	0·0213	237		
—— potash	KO, NO^5	101·2	2·058	Kp	0·0203	225	1, 1	231
			2·101	Kn	0·0207	230		
—— soda	NaO, NO^5	85·2	2·226	Kn	0·0261	290	1, $\frac{1}{3}$	294
—— silver	AgO, NO^5	170·1	4·355	Kn	0·0256	284	1, $\frac{1}{3}$	280
—— baryta	BaO, NO^5	130·6	3·185	Kn	0·0244	271	1, $\frac{1}{3}$	270
—— strontia	SrO, NO^5	106	2·810	Kn	0·0265	294	1, $\frac{1}{3}$	283
—— lead	PbO, NO^5	165·8	4·400	Kn	0·0265	294	1, $\frac{1}{3}$	291
Apatite	$CaCl + 3\,(3CaO, PO^5)$	526·6	3·225	Ms	0·0061	68		
Phosph. lead (native)	$PbCl + 3\,(3PbO, PO^5)$	1359·6	7·050	Ke	0·0052	58		
Arsen. lead (native)	$PbCl + 3\,(3PbO, AsO^5)$	1491	7·208	Ms	0·0408	53		

A	B	C Atom. Weight.	D E Spec. Grav.		F G Atom. Number.		H	I
hlorine	Cl, 10H O	125·4	1·200	Fd	0·0096	107	8,1	102
otash	K O, H O	56·2	2·100	Dt	0·0373	414	1, 1	415
oda	Na O, H O	40·2	2·000	Dt	0·0497	552	1, 1	552
.....	$Mn^2 O^3$, H O	88·2	4·328	Hd	0·0490	544		
boracic acid.	$B O^3$, 3H O	88·8	1·479	Kw	0·0166	184		
id with 1 At	$S O^5$, H O	49	1·845		0·0376	418	$\frac{2}{3}$, 1	422
.....	$S O^3$, 2H O	58	1·780	Dt	0·0317	352	$\frac{1}{2}$, 1	352
.....	$S O^3$, 3H O	67	1·632	Ur	0·0243	270	$\frac{1}{5}$, 1	269
with 1 At ..	$Se O^3$, H O	73	2·600	Mt	0·0356	395		
ith 1 At	$N O^5$, H O	63	1·521	Mt	0·0241	268		
.....	Ca O, $S O^3$, 2H O	86·5	2·322	R D	0·0268	298		
sulphate of	Mn O, $S O^3$, 4H O	120·6	2·091	Kp	0·0178	198		
ate of copper.	Cu O, $S O^3$, 5H O	124·8	2·274	Kp	0·0182	202		
sia	Mg O, $S O^3$, 7H O	123·7	1·751	Ms	0·0141	156		
.....	Zn O, $S O^3$, 7H O	143·2	2·036	Ms	0·0142	158		
.....	Ni O, $S O^3$, 7H O	140·6	2·037	Kp	0·0145	161		
and ammonia	$N H^4 O$, Mg O, $2S O^3$, 6H O	180·7	1·721	To	0·0095	105		
and ammonia	$N H^4 O$, Mn O, $2S O^3$, 6H O	195·6	1·930	To	0·0099	110		
d potash	K O, Zn O, $2S O^3$, 6H O	221·4	2·153	Kp	0·0097	108		
and ammonia	$N H^4 O$, Ni O, $2S O^3$, 6H O	197·6	1·915	Kp	0·0097	108		
sh	K O, Ni O, $2S O^3$, 6H O	218·8	2·123	Kp	0·0097	108		
and ammonia	$N H^4 O$, Cu O, $2S O^3$, 6H O	199·8	1·757	Kp	0·0088	98		
sh	K O, Cu O, $2S O^3$, 6H O	221	2·137	Kp	0·0096	107		
a and amm ..	$N H^4 O$, $Al^2 O^3$, $4S O^3$, 24H O	453·4	1·626	Kp	0·0036	40		
a and potash.	K O, $Al^2 O^3$, $4S O^3$, 24H O	474·6	1·724	Kp	0·0036	40		
m and potash	K O, $Cr^2 O^3$, $4S O^3$, 24H O	503·4	1·848	Kp	0·0037	41		
de of iron and	$N H^4 O$, $Fe^2 O^3$, $4S O^3$, 24H O	480·4	1·712	Kp	0·0036	40		
e acid.....	H F	19·7	1·061	Dv	0·0538	598		
.....	Ca F	39·2	3·150		0·0803	892		
of arsenic....	$As F^3$	131·3	2·730	Un	0·0207	230		
f sulphur	$S^2 Cl$	67·4	1·687	Dm	0·0250	278	1, $\frac{1}{4}$	278
f copper.....	$Cu^2 Cl$	99	3·678	Kn	0·0371	412	1, 0	414
f mercury ...	$Hg^2 Cl$	238·2	6·992	Kn	0·0293	325	1, 1	326
e of sulphur .	S Cl	51·4	1·620	Dm	0·0315	350	1, $\frac{3}{4}$	348
ac	N H^4 Cl	53·4	1·500	Kp	0·0281	312		
			1·528	Ms	0·0286	318		
otassium ...	K Cl	74·6	1·915	Kn	0·0257	285	1, $\frac{1}{4}$	292
			1·945	Kp	0·0260	289		
odium.....	Na Cl	58·6	2·078	Kn	0·0355	394	$\frac{1}{2}$, $\frac{3}{4}$	385
.....	Ag Cl	143·5	5·501	Kn	0·0383	425	1, 0	417
e of mercury.	Hg Cl	136·8	5·403	Kn	0·0395	439	$\frac{2}{3}$, 1	441
ead	Pb Cl	139·2	5·802	Kn	0·0418	461	$\frac{1}{2}$, $\frac{2}{3}$	466
arium.....	Ba Cl	104	3·704	Kn	0·0356	395		
			3·860	Bl	0·0371	412		
trontium....	Sr Cl	79·4	2·803	Kn	0·0353	392		
alcium	CaCl	55·9	2·040	Kn	0·0364	404		
			2·214	Bl	0·0396	440		
of phosphorus	$P Cl^3$	137·6	1·450	Dv	0·0105	117	2, $\frac{1}{3}$	117
uric acid....	$S O^2 Cl$	67·4	1·659	Rt	0·0674	749		
f of mercury.	$Hg^2 Br$	281·2	7·307	Kn	0·0260	289	1, $\frac{1}{4}$	287
otassium....	K Br	117·6	2·415	Kn	0·0205	228	2, $\frac{1}{4}$	227
ead	Pb Br	182·2	6·630	Kn	0·0363	403	$\frac{2}{3}$ 1	417
e of mercury.	Hg Br	179·8	5·920	Kn	0·0329	365	1, $\frac{3}{4}$	355
ilver	Ag Br	186·5	6·353	Kn	0·0340	378	$\frac{1}{2}$, 1	379
mercury	$Hg^2 I$	328·8	7·644	Kn	0·0232	258	1, $\frac{1}{2}$	259
assium.....	K I	165·2	2·908	Kn	0·0176	195	1, $\frac{3}{4}$	199
			3·104	Bl	0·0187	208		
d	Pb I	229·8	6·021	Kn	0·0262	291	1, $\frac{1}{4}$	295
f mercury ...	Hg I	227·4	6·200	Kn	0·0273	303	1, $\frac{1}{3}$	303
er	Ag I	234·1	5·026	Kn	0·0214	238	1, 2	241
			5·614	Bl	0·0240	267		
hydrogen ..	H S	17	0·900	Fd	0·0529	588	2, 3	578
of copper ...	$Cu^2 S$	79·6	5·977	Kn	0·0751	834	1, $\frac{1}{3}$	824

A	B	C Atom. Weight.	D	E	F	G	H	I
			Spec. Grav.		Atom. Number.			
Di-sulphuret of copper ...	Cu^2S	79·6	5·792	Hr	0·0728	809		
Sulphuret of manganese..	Mn S	43·6	4·000	Ms	0·0917	1019	1, 1	970
—— zinc	Zn S	48·2	3·923	Kn	0·0813	903	1, 1	878
—— cadmium	Cd S	71·8	4·605	Kn	0·0641	712	1, 1	768
			4·800	Bk	0·0668	742		
Protosulphuret of tin	Sn S	75	4·852	Kn	0·0647	719	1, $\frac{3}{4}$	789
			5·267	Bl	0·0702	780		
Sulphuret of lead	Pb S	119·8	7·505	Kn	0·0626	695	2, 0	694
—— nickel	Ni S	45·6	5·200	Gk	0·1140	1267		
Protosulphuret of copper .	Cu S	47·8	4·163	Kn	0·0871	968	1, 1	954
Cinnabar	Hg S	117·4	8·060	Kn	0·0686	762	1, $\frac{8}{10}$	757
Sulphuret of silver	Ag S	124·1	6·850	Kn	0·0552	613	1, 1	604
—— silver and copper ..	$Cu^2 Ag S^2$	203·7	6·255	St	0·0307	341		
Sulphuret of bismuth	$Bi^2 S^3$	260·8	7·000	Kn	0·0268	298	2, 1	295
Bisulphuret of carbon....	$C S^2$	38	1·272	Bz	0·0345	372	2, 8	373
Realgar	$As S^2$	107·2	3·544	Kn	0·0331	368	1, $\frac{2}{3}$	272
	$Mo S^2$	80	4·690	Hf	0·0586	651	1, $\frac{5}{6}$	642
Mosaic gold	$Sn S^2$	91	4·425	Bl	0·0488	542	1, $\frac{5}{6}$	551
			4·600	Kn	0·0505	561		
Iron pyrites.....	$Fe S^2$	59·2	5·183	Hf	0·0875	972	1, 1	964
Orpiment.....	$As S^3$	123·2	3·459	Kn	0·0280	311	1, $\frac{11}{12}$	310
			3·650	Bl	0·0296	329		
Tersulphuret of antimony	$Sb S^3$	177	4·334	Bl	0·0245	272	1, $\frac{2}{3}$	276
			4·752	Kn	0·0269	299		
Persulphuret of hydrogen	$H S^5$	81	1·769	Te	0·0218	242	6, 6	235
Cobalt-glance	Co As, $Co S^2$	166·4	6·298	Ms	0·0378	420		
Nickel-glance	Ni As, $Ni S^2$	166·4	6·294	Bt	0·0378	420		
Ruby silver (light)	$3Ag S, As S^3$	499·5	5·524	Ms	0·0111	124		
—— (dark).....	$3Ag S, Sb, S^3$	549·3	5·831	Ms	0·0106	118		

Although the numbers in column F bear to one another exactly the same ratio as those in G, and both may therefore be used for calculation, I have nevertheless in the following comparisons and calculations confined myself to the use of those in G, because these numbers admit of comparison not only with those of table, page 66, but also those of tables, pages 53 and 55. From this comparison of the tables we may draw the following conclusions :—

1. A space which will contain 1 atom of hydrogen in the gaseous state is capable of holding the following numbers of atoms of the following compounds according as they are or are not in the aeriform state; water 1 and 1234 ; carbonic acid 1 and 419; sulphurous acid 1 and 500; sulphuric acid 1 and 547; arsenious acid 2 and 420; oxide of chlorine $\frac{1}{2}$ and 247 ; hyponitric acid $\frac{1}{2}$ and 350 ; sal-ammoniac $\frac{1}{4}$ and 312 ; dichloride of mercury $\frac{1}{2}$ and 325 ; protochloride of mercury 1 and 439 ; terchloride of phosphorus $\frac{1}{2}$ and 117 ; chloro-sulphuric acid 1 and 749 ; dibromide of mercury $\frac{1}{2}$ and 289 ; proto-bromide of mercury 1 and 365 ; di-iodide of mercury $\frac{1}{2}$ and 258 ; prot-iodide of mercury 1 and 303 ; sulphuretted hydrogen 1 and 588 ; cinnabar $\frac{2}{3}$ and 762 ; bisulphuret of carbon 1 and 504. The highest degree of condensation that takes place in the passage of a body from the gaseous to the liquid or solid state amounts therefore to 1234 times (water) ; the lowest to 210 (arsenious acid). These numbers also show the incorrectness of the law enunciated by Persoz (page 57). Since 1 litre of vapour of water at 0° weighs 0·8003 grammes and 1 litre of water 1000 gr., Persoz, divides the weight in grammes of any compound in the gaseous state by 0·8003 in order to get the sp. gr. of the same compou[illegible]iquid or solid

state. In the case of sal-ammoniac this gives a correct result; for $\frac{1}{4} : 312 = 1 : 1248$, or according to Persoz, 1 litre of sal-ammoniac vapour weighing 1·196 grammes, $\frac{1 \cdot 196}{0 \cdot 8003} = 1 \cdot 49$ = sp. gr. of sal-ammoniac. But Persoz assumes in opposition to experiment that the 2-atomic vapour of arsenious acid and the 1-atomic vapour of sulphuret of carbon are $\frac{1}{2}$-atomic, and that the $\frac{1}{2}$-atomic vapour of calomel is $\frac{1}{4}$-atomic, in order to bring out results tolerably near the truth.

2. The atomic number of a compound is generally smaller than that of either of its elements. The only known exceptions to this rule are the following: potassium 245, potash 625, chloride of potassium 285; sodium 466, soda 999; chlorine 464, chloride of silver 425, proto-chloride of mercury 439, chloro-sulphuric acid 749. Such condensation therefore shows itself in those substances only which have the smallest atomic numbers, and but seldom even in these.

3. Ammermüller has shown that a compound of two substances may often have a new quantity of one of them added to it without perceptible alteration of volume, so that the sp. gr. of the compound increases just as much as the weight of the superadded substance, *e. g.*:

Cu^3	5·108	Cu^2	5·108	Hg^3	10·284	Hg^3	10·284
O	0·643	O^2	1·285	O	0·406	O^2	0·812
Sp. Gr.	5·751		6·393		10·696		11·096
Sn	5·846	Sn	5·846	Pb	7·437	Pb	7·437
O	0·793	O^2	1·586	O	0·573	O^2	1·146
Sp. Gr.	6·639		7·432		8·010		8·583

It appears from this that when 5·751 parts of suboxide of copper take up 0·643 more oxygen, without alteration of volume, the sp. gr. increases from 5·751 to 6·393, that is by 0·642, and similarly in the other three cases. With some compounds, however, it is necessary to multiply by a fraction in order to determine the sp. gr. of the higher compound from that of the lower, *e. g.*:

H	0·111	H	0·111	$1 \cdot 889 \cdot \frac{3}{4} = 1 \cdot 417$
O	0·889	O^2	1·778	
Sp. Gr.	1·000		1·889	

The observed sp. gr. of HO^2 is 1·452, which is still somewhat different from 1·417. In the case of Sn S and $Sn S^3$, Hg^2 Cl and Hg Cl, Hg^2 Br and Hg Br, the required factor, according to Ammermüller is $\frac{2}{3}$; in that of $As S^3$ and $As S^5$ it is $\frac{4}{5}$. These calculations, however, give nothing more than distant approximations to the sp. gr. determined by experiment. Moreover if we consider that in the case of suboxide of mercury, Herapath's determination of the sp. gr. which differs so widely from that of Karsten has been taken as the basis of the calculation, and in that of protoxide of lead, the very low determination of Le Royer and Dumas which was made upon the oxide in its vitreous state (and perhaps therefore containing silica), it appears very doubtful whether these few examples ought really to be taken as the foundation of a law, or whether they should not rather be regarded as purely accidental. On the other hand these relations may be most conveniently traced by means of the numbers in column G of the table. The atomic numbers are: of $Cu^2 O$ 892, of Cu O 1795, therefore nearly double, inasmuch as by the addition of 1 At. oxygen to 1 At. $Cu^2 O$, there are produced 2 At. Cu O; of $Hg^2 O$

from 472 to 563, of Hg O 1137, the same proportion therefore but not so exact; of Sn O 1101, of Sn O^2 from 983 to 1023; of Pb O 914 to 943, of Pb O^2 825 to 852, therefore nearly equal atomic numbers; of Hg^2 Cl 325, of Hg Cl 439, = 3 : 4; of Hg^2 Br 289, of Hg Br 365, = 4 : 5; of Hg^2 I 258, of Hg I 303, = 5 : 6; of Cu^2 S 834, of Cu S 968, = 6 : 7; of As O^3 403 to 425, of As O^5 360, = 15 : 14; of As S^2 368, of As S^3 311, = 5 : 4; but all these relations are merely approximate.

4. Kopp, like Le Royer and Dumas, makes use of atomic volumes (see page 57). He formerly determined the atomic volume of a compound by subjecting those of its elements to a complicated calculation by means of various coefficients: lately he has for the most part approximated to Schröder's method of calculation.

5. *Schröder's Theory of Volumes.* By dividing the equivalent of a substance by its specific gravity, Schröder obtains the *Equivalent volume*, which agrees with the atomic volume of Kopp in value but differs from it in signification, inasmuch as equivalent-volumes may be adopted even when the atomic theory is discarded. The meaning of the term has been already explained (page 57). The atomic volume or equivalent volume, is the reciprocal of the atomic number, so that if the atomic number = Z, the equivalent volume may be denoted by $\frac{1}{Z}$. Schröder's equivalent-volume or Kopp's atomic volume may be reduced to the atomic number as follows: Both are founded on the atomic weights of Berzelius (that of oxygen = 100). Thus, for example, the atomic weight of sulphur being 201·16 and its sp. gr. 1·98, its atomic volume is 201·16 : 1·98 = 101·6. If now the atomic weight of oxygen = 8 instead of 100, the equivalent-volume must be diminished in the ratio of 100 : 8, (100 : 8 = 101·6 : 8·126). Hence if the atomic weight of oxygen = 8, the equivalent volume of sulphur = 8·126: and dividing 1 by this number we obtain the atomic number of sulphur, viz. 0·1234. In the table, page 55, column D, the atomic number of sulphur is somewhat greater, viz. 0·1250, because the atomic weight from which it was determined was rather smaller and its sp. gr. greater. In order then to reduce the equivalent volume of Schröder to the atomic number, we must multiply by $\frac{8}{100}$ and divide 1 by the product; and conversely, the reciprocal of the atomic number given in this work, multiplied by $\frac{100}{8}$, gives the equivalent volume of Schröder. Now, according to Schröder, the equivalent volume of a compound is equal to the sum of the equivalent volumes of its elements, with this limitation, that in many cases the equiv. vol. of one or the other element requires to be multiplied by some factor either integral or fractional. The application of this law will be seen in the following examples, in which, however, for the sake of easier comparison, the atomic weights and specific gravities of the tables, pp. 55 and 68, have been used: this, however, makes no material difference, inasmuch as the equivalent volumes thus obtained merely require to be multiplied by $\frac{100}{8}$, in order to give almost exactly those employed by Schröder. The eq. vol. of carbon is 6 : 3·5 = 1·714; of sulphur 16 : 2·000 = 8; of zinc 32·2 : 6·9154 = 4·658; of lead 103·8 : 11·3889 = 9·114; of mercury 101·4 : 13·559 = 7·478. That of sulphuret of carbon is 38 : 1·272 = 29·874; of sulphuret of zinc 48·2 : 3·923 = 12·286; of sulphuret of lead 119·8 : 7·505 = 15·962; and of sulphuret of mercury = 14·566.

Now 1 eq. vol. zinc + 1 eq. vol. sulphur = 1 eq. vol. sulphuret of zinc, nearly (4·658 + 8 = 12·658). 8 eq. vol. carbon + 2 eq. vol. sulphur = 1 eq. vol. sulphuret of carbon (2 . 8 + 8 . 1·714 = 29·712); 1 eq.

vol. lead + $\frac{4}{5}$ eq. vol. sulphur = 1 eq. vol. sulphuret of lead (9·114 + $\frac{4}{5}$. 8 = 15·514); and $\frac{9}{10}$ eq. vol. mercury + 1 eq. vol. sulphur = 1 eq. vol. cinnabar (0·9 . 7·478 + 8 = 15·478).

Conversely, according to these principles, we may from the eq. vol. of a compound determine the eq. vol. and thence the sp. gr. of its elements, when the sp. gr. and thence the eq. vol. cannot be determined directly. In this manner Schröder makes use of the compounds of oxygen to determine the eq. vol. of that element in the solid state; this he finds = 33·8, which must be reduced to 2·704 if the atomic weight of oxygen be made = 8. According to this, 1 eq. vol. zinc + 1 eq. vol. oxygen = 1 eq. vol. oxide of zinc (4·658 + 2·704 = 7·362); if now we take Mohs' determination of the sp. gr. of oxide of zinc, viz., 5·432, we obtain 40·2 : 5·432 = 7·417 for the eq. vol. The eq. vol. of potash is obtained by adding $\frac{1}{3}$ of an eq. vol. of potassium (39·2 : 0·865 = 45·318) to 1 eq. vol. oxygen; we have then $\frac{1}{3}$. 45·318 + 2·704 = 17·210; the calculation of the eq. vol. from the sp. gr. of potash gives 47·2 : 2·656 = 17·771.

If atomic numbers be used instead of equivalent volumes, Schröder's method of calculation takes the following form. The equivalent volume of a substance is the reciprocal of its atomic number, that is, if the latter = Z, the former = $\frac{1}{Z}$. If now the eq. vol. of one element be denoted by $\frac{1}{Z'}$ and that of the other by $\frac{1}{Z''}$ we shall have for the sum of these magnitudes $\frac{Z''}{Z' Z''} + \frac{Z'}{Z' Z''} = \frac{Z' + Z''}{Z' Z''}$. Finally, since the atomic number is the reciprocal of the equivalent volume, the atomic number of the compound will be $\frac{Z' Z''}{Z' + Z''}$. Hence Schröder's mode of calculation, accommodated to the use of atomic numbers, gives the following rule: The atomic number of a compound is equal to the product of the atomic numbers of its two constituents divided by their sum. In those cases in which, according to Schröder's method, we should not simply add the equivalent volumes, but previously multiply one or both of them by integral or fractional factors, the same must be done in the altered form of the method when atomic numbers are used; the numerator of the above fraction will remain the same, viz., the product of the atomic numbers of the two elements, but the terms of the denominator must be multiplied by the same factors as those used in Schröder's original method, taken however in the reverse order*. Thus, in the case of sulphuret of carbon, Schröder's method requires the addition of 8 volumes of carbon and 2 of sulphur; according to the method now under consideration, the divisor consists of twice the atomic number of carbon + 8 times that of sulphur. A few examples will show the application of this method; the atomic numbers are those in table page 55, column F, and those in the last table, column G. The number in brackets is the atomic number obtained by dividing the specific gravity of the compound by its atomic weight and reduced to

* Let Z′ Z″ be the two atomic numbers, m', m'' the corresponding factors: then we have

$$m' \frac{1}{Z'} + m'' \frac{1}{Z''} = \frac{m' Z'' + m'' Z'}{Z' Z''}$$

the reciprocal of which, i.e. the atomic number of the compound is $\frac{Z' Z''}{m'' Z' + m' Z''}$ [W.]

the standard of hydrogen gas, as given in the last table, column G; it serves for comparison with the result of the calculation.

$$\begin{array}{lll} \mathrm{Zn\,S} & (2386 \,.\, 1388) : (\ 2386 + & 1388) = 878\ (903) \\ \mathrm{Ag\,S} & (1071 \,.\, 1388) : (\ 1071 + & 1388) = 604\ (613) \\ \mathrm{C\,S^2} & (6481 \,.\, 1388) : (2 \,.\, 6481 + 8 \,.\, & 1388) = 373\ (372) \end{array}$$

The results obtained by the application of this method to the more important compounds are given in columns H and I of the table. Column H shows the factors by which the terms of the divisor must be multiplied to obtain an approximate result. The number on the left applies to the atomic number of the element which goes first in the formula in column B; that on the right to the element which stands last in the same formula. Opposite cinnabar, for instance, we find 1, $\frac{9}{10}$; this shows that the product of the atomic numbers of mercury and sulphur must be divided by the atomic number of mercury + $\frac{9}{10}$ of that of sulphur. Column I gives the result of this calculation, which is to be compared with the atomic number in column G. The multipliers used are in some cases the same as those used by Schröder, in others different on account of differences in the specific gravities and atomic weights adopted in the calculation. The atomic number of oxygen has been assumed = 4200, that of hydrogen = 1747, and that of nitric acid = 364.

A survey of the table shows that the terms of the divisor must, in by far the greater number of instances, be multiplied by certain factors in order to obtain the desired quotients; and it is easy to see that if we are allowed to alter the divisor by multiplying its two terms by any whole numbers or fractions that we please to assume, we may always obtain a near approximation to the desired atomic number, whatever may be the product obtained by multiplying together the atomic numbers of the two constituent elements. The same remark applies to Schröder's method in its original form, in which the equivalent volumes before addition may be multiplied by any numbers or fractions whatever, and thus any desired sum may be produced. The multipliers which Schröder used in his calculations are 2, 3, 4, 6, 8, 15; $\frac{1}{2}$, $\frac{3}{2}$, $\frac{9}{2}$; $\frac{1}{3}$, $\frac{2}{3}$, $\frac{4}{3}$, $\frac{8}{3}$; $\frac{3}{4}$, $\frac{5}{4}$; $\frac{3}{5}$, $\frac{4}{5}$, $\frac{12}{5}$; $\frac{5}{6}$: and the use of these multipliers does not appear to follow any regular law. Although in looking over these very remarkable calculations of Schröder, it cannot fail to strike us that the equivalent volume of a compound is in many cases obtained by simple addition of those of its elements, the value so determined being very nearly equal to that which results from dividing the atomic weight by the specific gravity, still as the densities which give these results are not always those determined by the most trustworthy observations, and as in the greater number of cases, it is necessary to multiply by the most various numbers, it must remain doubtful, so long as these multipliers cannot be shown to follow any regular law, whether this mode of calculation rests upon any rational foundation.

6. Finally, I add my own method of considering these relations, which will at least serve to show that they admit of various modes of calculation. It may be expected that in the combination of 2 bodies of different atomic numbers, one of which tends to fill the space with a larger, the other with a smaller number of atoms, the result actually produced will be a mean between the two. Since however a compound atom occupies more space than a simple one, and more especially, since, by reason of the greater number of atoms composing it, its attraction for heat is stronger, and causes a more abundant collection of that element around it,—the interstitial spaces will from that cause be enlarged, and the number

of atoms in a given space probably diminished according to fixed laws. This diminution appears to vary as the square of the number of atoms which make up the compound atom; not however exactly, but subject in many cases to marked exceptions.

The following examples serve, as far as they go, to establish this view. In the combinations of 1 At. of a metal with 1 At. sulphur, this law would require us to add the atomic numbers of the metal and sulphur and divide the sum by 4, *i. e.*, the square of 2, since the compound atom consists of 2 simple atoms; but the divisor is never exactly 4, and varies from 3·6 to 4·6. Within the brackets is put for comparison the atomic number of the compound obtained by dividing the specific gravity by the atomic weight and reduced to the standard of hydrogen gas.

Sn S (1373 + 1388) : 3·6 = 767 (719 to 780)
Pb S (1218 + 1388) : 3·7 = 705 (695)
Ni S (3242 + 1388) : 3·7 = 1251 (1267)
Hg S (1485 + 1388) : 3·8 = 756 (762)
Ag S (1071 + 1388) : 4 = 602 (613)
Cd S (1719 + 1388) : 4·2 = 739 (710 to 742)
Zn S (2386 + 1388) : 4·2 = 899 (905)
Mn S (3220 + 1388) : 4·6 = 1002 (1019)
Cu S (3046 + 1388) : 4·6 = 964 (968)

In disulphuret of copper, Cu^2 S, 2 atoms of metal are combined with 1 At. sulphur: in bisulphurets, 1 atom of metal with 2 atoms of sulphur: and since in these compounds the number of simple atoms composing the compound atoms is 3, the divisor ought to be 9: it varies however, as follows:—

Cu^2 S (2 . 3046 + 1388) : 9 = 831 (834)
Fe S^2 (3203 + 2 . 1388) : 6 = 996 (972)
Mn S^2 (1991 + 2 . 1388) : 7 = 681 (651)
Sn S^2 (1373 + 2 . 1388) : 8 = 519 (542)
As S^3 (880 + 2 . 1388) : 10 = 366 (368)

In combinations of 1 At. metal with 3 At. sulphur, the divisor should be 4 . 4 = 16:

As S^3 (880 + 3 . 1388) : 16 = 315 (311)
Sb S^3 (576 + 3 . 1388) : 17 = 278 (272)

With 2 At. metal and 3 At. sulphur, the divisor should be 5 . 5 = 25:

Bi^2 S^3 (2 . 1024 + 3 . 1388) : 20 = 311 (298)

The mode of calculation being sufficiently exhibited in these examples, it will be enough in those which follow to give the chemical formula, the proper divisor, and the resulting atomic number, together with that found from the sp. gr. (in brackets):

K I : 3·5 = 193 (195).—Pb I : 5·6 = 295 (291).—Hg I : 6·3 = 305 (303).—Ag I : 6·3 = 239 (238).

Hg^2 I : 9 = 262 (258).

K Br : 3 = 223 (228).—Pb Br : 4 = 410 (403.)—Ag Br : 4 = 374 (378).

Hg^2 Br : 8 = 291 (289).

K Cl : 2·3 = 287 (285....289).—Na Cl : 3·2 = 384 (396).—Pb Cl : 3·5 = 467 (464).—Ag Cl : 3·5 = 424 (425).—Hg Cl : 4·4 = 432 (439). S Cl : 5 = 361 (351).

Cu^2 Cl : 9 = 431 (412).—Hg^2 Cl : 7 = 331 (325).—S^2 Cl : 11 = 290 (278).—P Cl^3 : 16 = 117 (117).

In the compounds of bromine and chlorine (the latter more particularly) the divisor is too much below its normal value, possibly because the atomic numbers of these compounds have been determined from their specific gravity in the liquid state and may therefore be too small. It is also worthy of remark that the divisor always has its smallest values in the combinations of potassium and sodium with iodine, bromine and chlorine; then follows lead, then silver and then mercury.

It is possible according to this view to calculate the hypothetical atomic number of oxygen from its combinations; but different compounds give widely different results, the numbers thus found varying from 1900 to 4100; and since, whatever number is assumed as the true one, the oxygen compounds exhibit relations differing from one another much more widely than those above considered, it seems better to leave this hypothetical part of the calculation on one side till the causes which may affect the magnitude of the divisor shall have been better ascertained. The great variation in the results will be seen from the following examples. Since according to the law under consideration the atomic number of a metallic oxide should be found by adding the atomic number of the metal to the atomic number of oxygen and dividing the sum by 4, (the oxide being supposed to contain 1 At. metal and 1 At. oxygen), it follows that if we multiply the atomic number of such a metallic oxide by 4 and subtract the atomic number of the metal from the product, the remainder will be the atomic number of oxygen. By treating different metallic oxides in this manner we obtain the following results: Potash; $(625 . 4) - 245 = 2251$. Soda; $(999 . 4) - 466 = 3520$. Oxide of zinc; $(1548 . 4) - 2386 = 3806$. Oxide of copper; $(1795 . 4) - 3046 = 4136$. Suboxide of copper $Cu^2 O$, in which there are 3 atoms and consequently the divisor $= \frac{1}{3}$, gives $(892 . 9) - 2 . 3046 = 1936$.

The same method applied to compounds of the second order gives the following results:

Anhydrous Carbonates. $Ba O, C O^2$ $(687 + 419) : 2{\cdot}3 = 481$ (484). $Sr O, C O^2 : 2{\cdot}3 = 547$ (543).—$Ca O, C O^2$ (Arragonite) $: 2{\cdot}5 = 660$ (664). $Pb O, C O^2 : 2{\cdot}5 = 533$ (533).—$Zn O, C O^2 : 2{\cdot}5 = 787$ (781 ... 790).—$Ag O, C O^2 : 2{\cdot}5 = 484$ (489).—$K O, C O^2 : 2{\cdot}8 = 373$ (363).—$Na O, C O^2 : 2{\cdot}8 = 507$ (514).—$Ca O, C O^2$ (Calcspar) $: 2{\cdot}8 = 590$ (599).—$Mg O, C O^2 : 2{\cdot}8 = 700$ (797).—$Mn O, C O^2 : 2{\cdot}8 = 673$ (684).—Here the divisor varies only from 2·3 to 2·8; that it is not equal to 4, may perhaps arise from the atomic number of carbonic acid having been calculated from its specific gravity in the liquid state: there can be no doubt that the sp. gr. and therefore also the atomic number of solid carbonic acid is much greater.

Anhydrous Sulphates. $Ba O, S O^3$ $(687 + 547) : 3{\cdot}1 = 388$ (400 ... 423). $Sr O, S O^3 : 3{\cdot}2 = 433$ (433).—$Pb O, S O^3 : 3{\cdot}3 = 451$ (451).—$Ca O, S O^3 : 3{\cdot}4 = 479$ (474).—$Ag O, S O^3 : 3{\cdot}5 = 382$ (380).—$K O, S O^3 : 3{\cdot}5 = 443$ (444).—$Na O, S O^3 : 3{\cdot}7 = 418$ (410).—$Zn O, S O^3 : 4{\cdot}5 = 473$ (471). $Mg O, S O^3 : 4{\cdot}7 = 482$ (477).—$Cu O, S O^3 : 4{\cdot}7 = 498$ (498).

Anhydrous Nitrates, the atomic number of nitric acid being hypothetically assumed $= 300$. $Ba O, N O^5$ $(687 + 300) : 3{\cdot}7 = 267$ (271). $Sr O, N O^5 : 3{\cdot}9 = 293$ (294).—$Ag O, N O^5 : 3{\cdot}9 = 279$ (284).—$K O, N O^5 : 4 = 231$ (233 ... 230).—$Pb O, N O^5 : 4{\cdot}2 = 300$ (294).—$Na O, N O^5 : 4{\cdot}4 = 263$ (250).

In all these three groups, the salts of baryta and strontia require the smallest divisors; then follow oxide of silver and potash, then soda, then magnesia; the position of lime, oxide of lead, and oxide of zinc is variable.

Hydrates. $K O, H O$ $(925 + 1234) : 4{\cdot}5 = 413$ (414).—$Na O,$

$HO : 4 = 558$ (552).—SO^3, $HO : 4{\cdot}2 = 424$ (418).—SO^3, $2HO : 12 = 251$ (252).—SO^3, $3HO : 16 = 265$ (270). These cases are nearly in accordance with the law; the divisor of SO^3, $2HO$ should however be 9 instead of 12. The first hydrate of nitric acid does not give so close an approximation: NO^5, HO $(300 + 1234) : 5{\cdot}7 = 269$ (268). For gypsum we have CaO, $SO^3 + 2HO$ $(474 + 2 . 1234) : 10 = 294$ (298), the divisor being 10 instead of 9.

The law thus developed may be expressed by the following formula:

$$\frac{x\,Z' + yZ''}{(x + y)^2} = Z'''$$

in which Z' denotes the atomic number of the first element, Z'' that of the second, Z''' that of the compound, x the number of atoms of the first element, y that of the second, which make up the compound atom. In the application of this law, striking deviations are apparent, as may be seen from the foregoing calculations. The most remarkable exception is presented by sulphuret of carbon, CS^2; $(6481 + 2{\cdot}1388) : 25 = 369$ (372); here the divisor is 25 instead of 9, as if the number of atoms in the compound were 5 instead of 3. Even allowing that many exceptions may arise, partly from errors in the supposed atomic weights of the simple substances, partly from incorrect determinations of the specific gravities of these simple substances and their compounds, the law must still be looked upon as far from the truth; it must needs be modified by many circumstances of much greater importance than those just noticed, and not till these circumstances have been discovered and reduced to calculation, shall we be able to regard the law as established on a proper foundation. The different degrees of cohesion in compounds and their elements, and their different attraction for heat would probably be found of particular importance.

It is to be wished that this matter could be subjected to careful mathematical analysis: the foregoing table might furnish the required data.

¶ The study of the relation between atomic weight and density has received some important additions since the publication of the last edition of this work. Of the researches of Kopp, Schröder, Löwig, and others of the continental chemists an elaborate account is given in the report of Professor Otto, a translation of which appears in the volume of Reports and Memoirs lately brought out by the Cavendish Society. The recent memoir of M. Filhol (*N. Ann. Chim. Phys.*, 21, 415), included in the same volume, likewise gives a review of the labours of previous experimenters in this branch of science, and adds some interesting results obtained by the author himself. I shall here notice some of the leading points in M. Filhol's memoir.

The author's calculations are founded on the following atomic weights and densities,—the latter determined by his own experiments.

Atomic Weights (O = 100)

Barium	854·85	Magnesium	157·75
Cadmium	696·17	Manganese	344·44
Calcium	250·00	Mercury	1250·90
Carbon	75·00	Potassium	488·84
Chlorine	443·02	Silver	1349·01
Chromium	249·83	Sodium	287·17
Copper	396·00	Strontium	545·60
Iodine	1585·57	Sulphur	200·00
Iron	350·00	Tin	735·03
Lead	1294·50	Zinc	406·59

Densities.

Iodic acid	4·250	Anhydrous sulphate of copper	3·530
Arsenious acid	3·884	,, ,, iron	2·841
Arsenic acid	4·250	,, ,, silver	5·410
Protoxide of barium	5·456	,, ,, lead	6·300
,, strontium	4.611	Nitrate of soda	2·260
,, calcium	3·180	,, baryta	3·200
,, aluminum	4·154	,, strontia	2·857
,, zinc	5·612	,, lime	2·240
,, lead	9·361	,, lead	4·581
Bi-oxide of copper (black oxide)	6·322	Hydrate of potash	2·044
Anhydrous chloride of potassium	1·994	,, soda	2·130
,, ,, sodium	2·240	,, baryta (Ba O, H O)	4·495
,, ,, barium	3·750	,, strontia (Sr O, H O)	3·625
,, ,, strontium	2·960	,, baryta (Ba O, 9H O)	1·656
,, ,, calcium	2·240	,, strontia (Sr O, 9H O)	1·396
,, ,, iron (Fe Cl)	2·528	,, zinc	3·053
Iodide of potassium	3·056	,, lime	2·078
,, sodium	3·450	Crystallized chloride of barium	2·664
,, barium	4·917	,, ,, strontium	1·603
,, lead	6·384	,, ,, calcium	1·635
,, mercury ($Hg I^2$)	6·250	,, ,, magnesium	1·558
,, silver	5·500	,, ,, iron	1·926
Monosulphuret of potassium	2·130	Crystallized sulphate of soda	1·520
,, sodium	2·471	,, ,, lime	2·331
Carbonate of potash	2·267	,, ,, magnesia	1·751
,, soda	2·509	,, ,, alumina	1·569
,, baryta	4·565	,, ,, iron	1·904
Anhydrous sulphate of potash	2·625	,, ,, zinc	2·036
,, ,, soda	2·629	,, ,, copper	2·286
,, ,, strontia	3·770	Crystallized nitrate of strontia	2·113
,, ,, lime	3·102	,, ,, lime	1·780
,, ,, magnesia	2·628	Anhydrous borax	2·367
,, ,, zinc	3·400	Crystallized borax	1·692

Most of these densities agree very well with those formerly determined by Boullay, Mohs, Karsten, &c., but there are some, *e.g.*, those of baryta and strontia, which differ considerably from former determinations, as will be seen by reference to the table pp. 68....72. Now it has been shown by Kopp that all the metals enter into combination without change of volume, with the exception of potassium, sodium, barium, strontium, magnesium, calcium and aluminum. With regard to barium and strontium, it must be observed that the volumes which Kopp assigned to these metals were deduced from the specific gravities of baryta and strontia as determined by Karsten. Filhol however shews that by adopting the densities given in the preceding table, barium and strontium may be removed from the list of exceptions. Thus the density of baryta being 5·456, its equivalent volume is $\frac{9.5}{5} \frac{4 \cdot 8.5}{4.5.6} = 175$, and estimating the volume of oxygen in these oxides at 32 (Kopp, *N. Ann. Chim. Phys.* 4,462) we have for the equivalent volume of barium, $175 - 32 = 143$. Similarly for strontium, the equivalent volume of strontia being $\frac{6.4}{4} \frac{5 \cdot 6.0}{6.11} = 140$, the equivalent volume of the metal is $140 - 32 = 108$: and these are the volumes with which, according to Kopp, the metals barium and strontium enter into other combinations.

Schröder has remarked that if from the equivalent volumes of a series of analogous compounds (oxides, chlorides, &c.) the volume of one of the elements be deducted, a constant remainder is obtained for the

element common to the whole series. On applying this process to nitrate of silver and nitrate of lead, and deducting the equivalent volumes of the metals contained in these salts, a constant remainder 358 is left for the radical NO^5. If on the other hand the equivalent volumes of the oxides be deducted, the silver salt gives for NO^5 the remainder 294, and the lead salt 326. Kopp regards this as an argument in favour of the theory of hydrogen-acids. Filhol however shows by numerous examples that with regard to a considerable number of salts, the subtraction of the volume of the base leaves a constant residue for the oxygen acid. Thus sulphuric acid appears to have two different volumes in combination: the sulphates of lead, baryta, potash, and strontia give for SO^3 the remainder 154, those of copper, zinc, lime, magnesia, and soda give 204.—The chromates of lead and potash give for CrO^3 the remainder 196.—The tungstates of lead and lime give $WO^3 = 212$.—The carbonates of cadmium, iron, manganese, lead, zinc, baryta, lime, magnesia, potash, soda, strontia, and and the double carbonate of lime and magnesia, give for carbonic acid the volume 119; and lastly, the nitrates of lead, ammonia, potash, soda, baryta and strontia give for NO^5 the volume 326. The discrepancy which occurs in the case of nitrate of silver is attributed by Filhol to an error in the determination of the density of oxide of silver. On the whole therefore, the results of these calculations cannot be regarded as decidedly favourable to either theory of the constitution of salts in preference to the other.

Filhol likewise points out some remarkable relations with regard to the changes of volume which take place in combination. Thus with regard to the chlorides: let P denote the atomic weight of chlorine, d its density; P′ the atomic weight of the metal, d' its density; and Δ the density of the chloride on the supposition that the elements unite without change of volume: then $\Delta = \dfrac{(P + P')\,dd'}{Pd' + P'd}$

If now D denote the density of the chloride determined by experiment, we always find $D > \Delta$, and $\dfrac{D - \Delta}{D}$ expresses the coefficient of contraction.

The same method is applicable to other compounds (sulphates, carbonates, &c). The following table contains a series of results obtained in this manner. The density of chlorine is estimated at 1·35, being the mean of the results obtained by Faraday and Karsten, viz. 1·33 and 1·38; that of carbonic acid at 0·83.

Name of Compound.	Density by Calculation.	Density by Experiment.	Coefficient of Contraction.
1. *Chlorides.*			
Potassium	1·039	1·994	0·478
Sodium	1·169	2·240	0·477
Barium	2·825	3·750	0·265
Strontium	2·266	2·960	0.234
Calcium	1·702	2·240	0·240
Lead	3·928	5·541	0·291
Silver	3·920	5·530	0·291

Name of Compound.	Density by Calculation.	Density by Experiment.	Coefficient of Contraction.
2. *Sulphates.*			
Magnesia	2·266	2·628	0·137
Zinc	2·920	3·400	0·140
Copper	2·991	3·530	0·152
Baryta	3·393	4·440	0·236
Strontia	2·901	3·770	0·230
Lime	2·366	3·102	0·245
Lead	4·729	6·300	0·249
3. *Carbonates.*			
Baryta	2·566	4·565	0·437
Strontia	1·949	3·610	0·460
Lime	1·415	2·720	0·477
Lead	3·491	6·470	0·459
Cadmium	2·783	4·455	0·380
Magnesia	1·293	2·966	0·563
Manganese	1·264	3·691	0·657
Zinc	1·860	4·445	0·581
4. *Hydrates.*			
Baryta (Ba O, H O)	3·718	4·495	0·172
Strontia (Sr O, H O)	2·989	3·625	0·175
Lime (Ca O, H O)	2·292	2·078	0·093
Magnesia (Brucite)	2·336	1·920	0·178
Alumina (Gypsite)	2·400	1·989	0·171
Alumina ($Al^2 O^3$, 8H O)	1·786	1·459	0·183
Zinc (Zn O, H O)	3·434	3·053	0·110
Baryta (Ba O, 9H O)	2·288	1·656	0·276
Strontia (Sr O, 9H O)	1·911	1·396	0·269
5. *Crystallized Sulphates.*			
Soda	1·520	1·375	0·093
Magnesia	1·751	1·434	0·180
Lime	2·331	2·099	0·099
Zinc	2·036	1·658	0·171
Iron	1·904	1·546	0·188
Copper	2·286	1·829	0·199
6. *Crystallized Chlorides.*			
Strontium	1·920	1·603	0·165
Barium	3·160	2·640	0·165

It will be seen from this table that in a very large number of cases, independently of all hypothesis, the coefficients of contraction of those compounds which most strongly resemble one another in a chemical point of view, are sensibly the same.

It may likewise be observed that in a certain number of cases the ratio between the calculated densities of certain compounds of the same kind is the same as that which exists between the densities determined by experiment. Hence we may calculate, *à priori*, the densities of certain salts according to those of their elements and that of a salt of the same species

having a close analogy to the former: In such a case we have in fact—$\Delta : \Delta' :: D : D'$;—thus for

Chloride of sodium ..... $\Delta = 1{\cdot}169$, $D = 2{\cdot}24$
„ potassium.... $\Delta' = 1{\cdot}029$
and $1{\cdot}169 : 1{\cdot}039 :: 2{\cdot}24 : 1{\cdot}990$

The density of the latter salt by experiment is 1·994 (*vid.* p. 80); according to Karsten it is 1·915, according to Kopp, 1·945.—Again for

Sulphate of baryta..... $\Delta = 3{\cdot}393$, $D = 4{\cdot}44$
„ strontia .... $\Delta' = 2{\cdot}901$
and $3{\cdot}393 : 2{\cdot}901 :: 4{\cdot}44 : 3{\cdot}796$

The experimental result is 3·77; Karsten makes it 3·59, Breithaupt 3·95.

Other examples might be adduced, but the relation thus developed is not sufficiently general to constitute a law.

In conclusion, M. Filhol remarks that the subject of the relation between atomic weight and density is not so far advanced as has been imagined,—that it is easy by slightly altering the numbers which form the bases of these calculations to obtain results of very fascinating uniformity: but this very circumstance ought to create distrust of such results; for it is extremely difficult—considering the great number of causes of error, often inevitable, which beset these calculations—to attain that degree of exactness which apparently belongs to many of the results which have been put forth in connection with this subject.

A series of elaborate memoirs on atomic volume and specific gravity has been published by Messrs. Playfair and Joule in the Memoirs and Quarterly Journal of the Chemical Society of London. (*Chem. Mem.* 2, 477; 3, 54 and 199; *Qu. J. of Chem. Soc.* 1, 121.) The principal results contained in these memoirs are as follows.

I. *The volumes of salts in solution are either equal to each other, or are multiples one of the other.*

If 9, the atomic volume of water (atomic weight of hydrogen = 1) be assumed as the standard of comparison, this law may also be thus expressed: *Compounds dissolved in water increase its volume either by* 9 *or by multiples of* 9.

a. Certain salts, such as the magnesian sulphates, the alums, &c., dissolve in water without increasing its bulk more than is due to the liquefaction of the water which they themselves contain.

b. Anhydrous salts, or salts containing a small proportion of water occupy in solution a number of volumes, which pass along with them unchanged into their union with other salts.

c. The volume occupied by double salts when dissolved is (with certain exceptions) the sum of the volumes occupied by their constituents when separate.

II. *The volumes of solid bodies bear a simple relation to each other, being multiples of a certain submultiple of the volume of ice.*

The density of ice as determined by Playfair and Joule is 0·9184, which agrees almost exactly with the number 0·9180 determined by Brunner (*N. Ann. Chim. Phys.* 14, 369). Hence the atomic volume of ice $= \frac{9}{0{\cdot}9184} = 9{\cdot}8$. This being determined, the submultiple in question adopted by the authors as the unit of volume for solids is $\frac{9{\cdot}8}{8} = 1{\cdot}225$; so that the atom of ice, considered as a globe or cube, will have twice the linear dimensions of the atom possessing this unit-volume. In some cases the volumes of solid bodies correspond more nearly to multiples of

$\frac{1\cdot225}{2} = 0\cdot6125$ than of 1·225 itself: but these cases being comparatively few are regarded as exceptional. The following table gives the atomic volumes, &c. of some of the metals in a finely divided state; also of flowers of sulphur.

Name.	Atomic Weight.	Volume by experiment.	1·225 as Unity.	Volume by theory.	Sp. Gr. by theory.	Sp. Gr. by experiment.
Copper.....	31·65	3·757	3	3·675	8·612	8·424
Cobalt	29·57	3·701	3	3·675	8·047	7·989
Nickel	29·62	3·782	3	3·675	8·060	7·832
Iron	27·18	3·812	3	3·675	7·396	7·130
Arsenic	37·67	7·203	6	7·350	5·125	5·230
Sulphur	16·03	8·380	7	8·575	1·870	1·913
Platinum	98·84	5·563	$4\frac{1}{2}$	5·512	17·931	17·766
Uranium	217·26	25·790	21	25·725	8·445	8·425
Magnesium	12·69	5·665	$4\frac{1}{2}$	5·512	2·302	2·240

The volumes of the metals in their more compact state do not accord very well with the law above stated, probably from the effect of cohesion.

The volume of the magnesian oxides in their most compact state, is found to be very nearly $5 \times 1\cdot225 = 6\cdot12$. Hence that of oxygen in these oxides must be $2 \times 1\cdot225 = 2\cdot45$*.—Now the volume of sulphur is 8·57; consequently, that of sulphuric acid, SO^3, will be $8\cdot57 + 3 \times 2\cdot45 = 15\cdot92$. Again the mean sp. gr. of sulphate of soda, as determined by various experimenters, is 2·562: this gives 27·9 for the atomic volume of that salt; and deducting 15·9 the volume of sulphuric acid, we have 12 for the atomic volume of soda: this is nearly $10 \times 1\cdot225 = 12\,25$.—The volume of potash (deduced from the sp. gr. 2·756 determined by Karsten) is 17·75, which is not far from $14 \times 1\cdot225 = 17\cdot15$.—The volume of anhydrous sulphate of ammonia is 39·2 (*Chem Mem.* 2, 428), from which deducting 15·9 for the acid, we have left 23·3 as the volume of oxide of ammonium. This is very nearly $18 \times 1\cdot225 = 23\cdot27$.—Aluminum has a density of 2·5 (Wöhler): this gives 5·47 for its atomic volume, making it nearly equal to $4\frac{1}{2} \times 1\cdot225$ or 5·5. Chromium has the density 5·1 which makes its atomic volume = 5·5: and admitting that in the sesqui-oxides oxygen enters with the volume $3 \times 1\cdot225 = 3\cdot675$, we shall have for the volumes of alumina and oxide of chronium $5\cdot51 \times 2 + 3\cdot675 \times 3 = 22\cdot05$.—Sesqui-oxide of iron being isomorphous with alumina and oxide of chromium its volume in combination may likewise be assigned as 22·05. The reason for selecting the particular results detailed in this paragraph will be seen immediately. The volumes assigned to alumina and the sesqui-oxides of iron and chromium, must be regarded as to a considerable extent hypothetical.

III. In highly hydrated salts the water of crystallization always occupies the volume of ice.

a. In the class of hydrated arseniates and phosphates with 24 atoms of water of crystallization, and in carbonate of soda with 10 atoms of water, neither acid nor base occupies any appreciable space, the volume of

* This agrees very nearly with the number 32 assigned by Kopp (whose numbers are based on the oxygen scale of atomic weights) for the atomic volume of oxygen: for $32 \times \frac{8}{100} = 2\cdot56$. (W.)

the salt being the same as that of the *water of crystallization* rozen into ice.

b. In cane and milk-sugar the carbon ceases to occupy space, the hydrogen and oxygen taking up exactly the space of the corresponding quantity of water frozen into ice.

These results are exhibited in the following table. It is especially remarkable that in the ordinary phosphate and arseniate of soda, the atom of basic water disappears as well as the two atoms of soda.

Name.	Formula.	Atomic Weight.	Volume by experiment.	9·8 or volume of ice as unity.	Volume by theory.	Sp. Gr. by theory.	Sp. Gr. by experiment.
Carbonate of soda	$NaO, CO^2 + 10HO$	143·4	98·6	10	98·0	1·463	1·454
Phosphate of soda	$2NaO, HO, PO^5 + 24HO$	359·1	235·5	24	235·2	1·527	1·525
Sub-phosphate of soda	$3NaO, PO^5 + 24HO$	381·6	235·2	24	235·2	1·622	1·622
Arseniate of soda	$2NaO, HO, AsO^5 + 24HO$	402·9	232·0	24	235·2	1·713	1·736
Sub-arseniate of soda	$3NaO, AsO^5 + 24HO$	425·2	235·6	24	235·2	1·808	1·804
Cane-sugar	$C^{12} H^{11} O^{11}$	171	107·4	11	107·8	1·586	1·593
Milk-sugar	$C^{24} H^{24} O^{24}$	360	234·7	24	235·2	1·531	1·534

IV. Another class of salts including all the hydrated magnesian sulphates, sulphate of alumina, borax, pyrophosphate of soda, and the alums, possess a volume made up of that of their bases and of their solid water, their acids ceasing to be recognizable in space.

Table A.

Salts.	Formula.	Atomic weight.	Space occupied by solid water.	Space occupied by base.	Sum of spaces occupied by base and water.	Vol. of salt by exp.	Sp. gr. by theory.	Sp. gr. by exp.
Sulphate of copper ..	$CuO, SO^3 + 5HO$	124·66	49·00	6·12	55·12	54·7	2·261	2·279
Sulphate of zinc	$ZnO, SO^3 + 7HO$	143·43	68·6	6·12	74·72	74·2	1·919	1·931
Sulphate of magnesia	$MgO, SO^3 + 7HO$	123·67	68·6	6·12	74·72	73·5	1·655	1·683
Sulphate of iron	$FeO, SO^3 + 7HO$	139·0	68·6	6·12	74·72	73·58	1·860	1·888
Sulphate of nickel ..	$NiO, SO^3 + 6HO$	131·74	58·8	6·12	64·92	64·6	2·029	2·037
Sulphate of soda	$NaO, SO^3 + 10HO$	161·48	98·0	12·25	110·25	109·9	1·464	1·469
Sulphate of alumina .	$Al^2O^3, 3SO^3 + 18HO$	333·7	176·4	22·05	198·45	199·6	1·681	1·671
Biborate of soda	$NaO, 2BO^3 + 10HO$	191·23	98·0	12·25	110·25	110·5	1·734	1·730
Pyrophosphate of soda	$2NaO, PO^5 + 10HO$	224·15	98·0	24·50	122·50	122·0	1·829	1·836

Table B.

Salts.	Formula.	Atomic weight.	Vol. of solid water.	Vol. of proper metallic base.	Vol. of alkaline base.	Sum of vols. of water and base.	Vol. by exp.	Theoretical sp. gr.	Sp. gr. by exp.
Potash alum ..	$Al^2O^3, 3SO^3 + KO, SO^3 + 24HO$	476·38	235·2	22·05	17·15	274·4	274·0	1·736	1·731
Ammonia alum	$Al^2O^3, 3SO^3 + NH^4O, SO^3 + 24HO$	455·38	235·2	22·05	23·27	280·52	280·2	1·623	1·625
Chrome alum .	$Cr^2O^3, 3SO^3 + KO, SO^3 + 24HO$	503·3	235·2	22·05	17·15	274·4	273·1	1·834	1·843
Ammonia iron alum	$Fe^2O^3, 3SO^3 + NH^4O, SO^3 + 24HO$	481·03	235·2	22·05	23·27	280·52	280·5	1·714	1·715

It will be seen from these tables that many salts contain one atom of water of crystallization for every unit-volume in their base. Thus sulphate of alumina possesses 18 atoms of water, and the volume of its base is $18 \times 1{\cdot}225$. Sulphate of soda has ten atoms of water, and the volume of its base is $10 \times 1{\cdot}225$. Biborate of soda also crystallizes with 10 atoms of water. The magnesian sulphates generally crystallize with 7 atoms of water: of these however 2 atoms are united by a much less powerful affinity than the rest, being driven off by a heat of 212°, and even under certain circumstances escaping in dry air at ordinary temperatures. The number of atoms of water essential to the crystallized salt may therefore be estimated at 5, which is the actual number contained in the ordinary crystals of sulphate of copper. The volume of the base of these salts is $5 \times 1{\cdot}225$. Now the volume of solid water being 9·8 and the unit-volume of the base 1·225, it follows that the volume of the salt (in which the acid does not appear) must be a multiple of $9{\cdot}8 + 1{\cdot}225$, that is of 11·025. In the first series of researches by Messrs. Playfair and Joule (*Chem. Mem.* vol. II. p. 401) numerous tables are given showing that in many classes of salts—sulphates, chlorides, oxalates, &c. the volume in the solid state is a multiple of 11 or of some number very near it. The explanation of this fact is contained in what has just been stated. ¶

b. State of Aggregation.

A compound is at ordinary temperatures either solid, liquid or gaseous.

I. A solid compound may be formed:

1. From two gases. *Condensation.*—Hydrochloric acid gas forms a solid compound with ammoniacal gas, viz. sal-ammoniac.

2. From a gaseous and a liquid body. *Absorption.*—Mercury absorbs chlorine and oxygen gases, forming solid compounds.

3. From a gaseous and a solid body. *Absorption* again.—Iron and other solid metals absorb oxygen gas, and hydrate of soda absorbs carbonic acid gas.

4. From two liquids.—Mercury and bromine.

5. From a liquid and a solid.—Mercury forms solid amalgams with several metals; burnt lime mixed with $\frac{1}{3}$ its weight of water crumbles to solid hydrate of lime; burnt gypsum mixed with water hardens into the state of gypsum combined with water of crystallization.

6. From two solids, generally by fusion.—The combinations of metals with one another or with sulphur.

II. A liquid compound may be formed:

1. From two gases. *Condensation.*—Hydrogen and oxygen gases combine and form water.

2. From a gas and a liquid. *Absorption.*—Water absorbs hydrochloric acid gas forming solution of hydrochloric acid.

3. From a gas and a solid. *Absorption.*—Arsenic, antimony, or tin absorbs chlorine gas, forming a liquid metallic chloride.

4. From two liquids. *Mixture in its most confined sense.*—Water and alcohol; sulphuret of carbon and chloride of sulphur.

5. From a solid substance and one that is liquid at the ordinary or a somewhat higher temperature. *Solution in the wet way.*—Salts and water, camphor and spirit of wine, sulphur and fatty matters, lead and mercury.

6. From two solids.—Sometimes in the cold, as common salt and ice,

bismuth-amalgam and lead-amalgam; sometimes not below a red heat, as carbon and sulphur.

III. A compound gaseous at the ordinary temperature and pressure of the air arises only:

1. From two permanent gases.—Hydrogen and chlorine.
2. From a permanent gas and a liquid.—Hydrogen gas and bromine.
3. From a permanent gas and a solid.—Hydrogen gas and sulphur; oxygen gas and carbon.

Since no compound which is gaseous at ordinary pressures and temperatures is ever formed by the combination of two liquids or two solids or a solid and a liquid, while on the contrary solid and liquid compounds are formed by the union of two permanent gases, it may be surmised that if any of the hitherto undecomposed bodies are really compound, such will probably be found among the solid and liquid classes.

The less completely the mutual affinity of ponderable bodies is satisfied, or in other words, the less complicated the combinations which they form, the stronger is their attraction for heat and the greater their elasticity; those elements which are gaseous under ordinary circumstances have also on an average the smallest atomic weights.

c. Crystalline Form.

The crystalline form of a compound probably bears a definite relation to that of its elements. Such a relation however has not yet been completely traced out, partly because the crystalline forms of many important elements, oxygen for instance, are unknown,—partly because one and the same substance, simple or compound, often assumes one or another crystalline form according to circumstances, *i.e.* exhibits *Dimorphism.* (q. v.) The existence of such a relation is however apparent from the facts by which Mitscherlich has established his important theory of *Isomorphism.* The term *Isomorphous* in its widest sense applies to those bodies which can replace one another in a compound without producing any alteration in the crystalline form of that compound, except small angular differences. Such bodies may be divided into the following groups.

A. *Substances which are isomorphous both in the separate state and in combination.*—Substances possessing the same crystalline form and replacing one another in combination according to equal numbers of atoms without alteration of crystalline form. Arsenic and antimony crystallize in acute rhombohedrons: $As O^3$ exhibits the same crystalline form as $Sb O^3$, and many double salts containing $As O^3$ as one base, present, according to Mitscherlich, the same crystalline form as the corresponding salts in which $As O^3$ is replaced by $Sb O^3$.

B. *Substances which replace one another in compounds according to equal number of atoms.* The crystalline form of such substances in the separate state is either different or else unknown; but they replace one another in combinations according to equal numbers of atoms and without alteration of crystalline form. Titanium crystallizes in cubes, tin in regular six-sided prisms; but both $Ti O^2$ and $Sn O^2$ crystallize in square prisms. The crystalline forms of lime and magnesia are unknown, but $Ca O$, $C O^2$ and $Mg O$, $C O^2$ crystallize in obtuse rhombohedrons. This group of substances may perhaps be hereafter shown to be identical with the first, when we shall have become acquainted with the crystalline forms of these bodies in the separate state and, possibly have discovered that their difference of form may be referred to Dimorphism.

C. *Substances which replace one another in combination according to*

unequal numbers of atoms.—It sometimes happens that one atom of an element contained in a compound is replaced by two or more atoms of another element, or by two other elements without alteration of crystalline form. Hyperchlorate of potash (KO, ClO^7) has the same form as hypermanganate of potash (KO, Mn^2O^7); here 1 At. chlorine is replaced by 2 At. manganese. Sal-ammoniac (NH^4Cl) crystallizes in the same form as chloride of potassium; hence K and NH^4 are isomorphous. In such cases no such chemical resemblance exists between the interchangeable bodies as in cases A and B: thus manganese bears no resemblance to chlorine, nor does nitrogen to potassium.

The following is a general view of the several groups of simple and compound substances which exhibit the same crystalline form with or without slight differences of angular magnitude. Each group of isomorphous substances is distinguished by a number: if it contains bodies of different stoichiometrical nature it is further subdivided by means of letters. The same substance, if dimorphous or trimorphous, may be repeated in different groups. Mitscherlich's observations are denoted by *Mt.*

Regular System.

1. *Homohedral.* *a.* C (Diamond) P, K, Ti, Bi, Cd, Pb, Fe, Cu, Ag, Au.

b. Co As, Zn S, Pb S, Co S, Ag S, K I, Na I, K Br, Na Br, NH^4Cl, K Cl, Na Cl, L Cl, Ag Cl, K F, Na F, Ca F.

c. Cu^2O, Cu^2S, Cu^2Cl, Hg^2Ag.

d. AsO^3, SbO^3, *Wöhler.*

e. MgO, Al^2O^3, (Spinell),—MgO, Fe^2O^3, (Pleonast),—ZnO, Al^2O^3, (Gahnite),—ZnO, Fe^2O^3, (Franklinite),—FeO, Fe^2O^3, (Magnetic iron ore). *Abich.*

f. BaO, NO^5,—SrO, NO^5,—PbO, NO^5, and according to Berzelius, PbO, NO^3.

g. $NH^4Cl, PtCl^2$,—$NH^4Cl, IrCl^2$,—$KCl, PtCl^2$,—$KCl, IrCl^3$—$KCl, OsCl^2$. *Berzelius.*

h. $NH^4O, Al^2O^3, 4SO^3, 24Aq$.—$NH^4O, Cr^2O^3, 4SO^3, 24Aq$.—$NH^4O, Mn^2O^3, 4SO^3, 24Aq$.—$NH^4O, Fe^2O^3, 4SO^3, 24Aq$.—$KO, Al^2O^3, 4SO^3, 24Aq$.—$KO, Cr^2O^3, 4SO^3, 24Aq$.—$KO, Mn^2O^3, 4SO^3, 24Aq$.—$KO, Fe^2O^3, 4SO^3, 24Aq$.—$NaO, Al^2O^3, 4SO^3, 24Aq$. *Mt.*

i. $KO, Al^2O^3, 4SiO^2$, (Leucite).

k. $NaO, Al^2O^3, 4SiO^2, 2Aq$, (Analcime).

2. In pentagonal dodecahedrons: FeS^2 (Iron pyrites).—Co^3AsS^2 (Cobalt-glance).

Four-membered or *Square Prismatic System.*

3. CaO, WO^3,—PbO, WO^3,—PbO, MoO^3, *Levy* (*Pogg.* 8, 513),—PbO, CrO^3. *Johnston.*

4. $NiO, SO^3, 7Aq$.—$NiO, SeO^3, 7Aq$.—$ZnO, SeO^3, 7Aq$. *Mt.*

5. $NH^4O, 2HO, PO^5$,—$NH^4O, 2HO, AsO^5$,—$KO, 2HO, PO^5$,—$KO, 2HO, AsO^5$. *Mt.*

6. $3CuO, 2Ur^2O^3, 3PO^5, 24Aq$.—$3CaO, 2Ur^2O^3, 3PO^5, 24Aq$.

7. $2NH^3, AgO, SO^3$,—$2NH^3, AgO SeO^3$,—$2NH^3, AgO, CrO^3$. *Mt.*

8. *a.* $CuFeS^2$ (Copper pyrites).—*b.* Mn^2O^3 (Braunite). *Kobell.*

9. TiO^2 (Rutile),—SnO^2 (Tinstone).

10. *a.* $Ti O^2$ (Anatase).
b. $K O, 8Ca O, 15Si O^2, 16Aq$ [?] (Apophyllite). *Kobell.*
11. *a.* $2Zr O, Si O^2$ (Zircon).
b. $3Ca O, 2Al^2 O^3, 5Si O^2$ [?] (Wernerite). *Breithaupt.*

Two-and-two-membered or *Right Prismatic System.*

12. Sulphur.—Iodine.
13. $As O^3$,—$Sb O^3$. Wöhler.
14. *a.* $Fe S^2$ (White iron pyrites).—*b.* $Fe^2 As S^2$ (Arsenical pyrites).
15. *a.* $Mn^2 O^3, H O$ (Manganite).
b. $2Ca O, Al^2 O^3, 3Si O^2, Aq$ [?] (Prehnite). *Kobell.*
16. *a.* $Ca O, CO^2$ (Arragonite),—$Ba O, CO^2$,—$Sr O, CO^2$,—$Pb O, CO^2$.
b. $K O, N O^5$.
17. *a.* $Ba O, S O^3$,—$Sr O, S O^3$,—$Pb O, S O^3$. *Mt.*
b. $N H^4 O, Cl O^7$,—$N H^4 O, Mn^2 O^7$,—$K O, Cl O^7$,—$K O, Mn^2 O^7$. *Mt.*
18. *a.* $Na O, S O^3$,—$Na O, Se O^3$,—$Ag O, S O^3$,—$Ag O, Se O^3$ (*fig.* 59). *Mt.*
b. $Ba O, Mn^2 O^7$. *Mt.*
19. *a.* $K O, S O^3$,—$K O, Se O^3$,—$K O, Cr. O^3$,—$K O, Mn O^3$ (*fig.* 76). *Mt.*
b. $N H^4 O, S O^3, Aq$. *Mt.*
20. *a.* $Mg O, S O^3, 7Aq$,—$Zn O, S O^3, 7Aq$,—$Ni O, S O^3, 7Aq$,—$Mg O, Se O^3, 7Aq$,—$Zn O, Se O^3, 7Aq$ (*fig.* 71, 72, 73). *Mt.*
b. $Sb S^3$. *Kobell.*
21. $Na O, P O^5, 4Aq$,—$Na O, As O^5, 4Aq$ (*fig.* 64). *Mt.*
22. $2Mn O, Si O^2$ (Chrysolite),—$2Mn O, Si O^2$. *Berthier.*
23. $Na O, Al^2 O^3, 3Si O^2, 2Aq$ (Natrolite),—$Ca O, Al^2 O^3, 3Si O^2, 3Aq$ (Skolezite).
24. $Ba O, C^4 H^3 O^3, 3Aq$ (Acetate of baryta),—$Pb O, C^4 H^3 O^3, 3Aq$ (Acetate of lead), (*fig.* 60). *Mt.*
25. $K^3 Fe^2 Cy^6$,—$K^3 Co^2 Cy^6$

Two-and-one-membered or *Oblique Prismatic System.*

26. *a.* Sulphur.
b. $K O, 2S O^3, H O$,—$K O, 2Se O^3, H O$. *Mt.*
27. $Fe O, Ta O^3$ (Tantalite),—$Fe O, W O^3$ (Wolfram). *Breithaupt.*
28. $Ca O, S O^3, 2Aq$,—$Ca O, Se O^3, 2Aq$. *Mt.*—$Fe O, S O^3, 2Aq$. *Graham.*
29. $Fe O, S O^3, 6Aq$,—$Co O, S O^3, 6Aq$,—$Mn O, S O^3, 6Aq$,—$Co O, Se O^3, 6Aq$,—Mixtures of $Fe O, S O^3$, with $Cu O, S O^3$, or with $Zn O, S O^3$; similarly of $Cu O, S O^3$, with $Zn O, S O^3$, or with $Ni O, S O^3$, or with $Mg O, S O^3$; similarly of $Mn O, S O^3$, with $Mg O, S O^3$, or with $Zn O, S O^3$, always in combination with 6 At. water (*fig.* 111). *Mt.*
30. $Mg O, S O^3, 7Aq$,—$Zn O, S O^3, 7Aq$,—$Co O, S O^3, 7Aq$,—$Ni O, S O^3, 7Aq$,—$Mg O, Se O^3, 7Aq$,—$Co O, Se O^3, 7Aq$. *Mt.*
31. $Na O, S O^3, 10Aq$,—$Na O, Se O^3, 10Aq$,—$Na O, Cr O^3, 10Aq$ (*fig.* 118, 119). *Mt.*
32. $2N H^4 O, P O^5, H O$,—$2N H^4 O, As O^5, H O$, (*fig.* 93, 94, 95). *Mt.*
33. $2Na O, P O^5, 25Aq$,—$2Na O, As O^5, 25Aq$, (*fig.* 96—100). *Mt.*
34. *a.* $Na O, 2B O^3, 10Aq$, (Borax).
b. $Ca O, Mg O, 2Si O^2$, (Augite),—$Na O, 2Fe O, 4Si O^2$ [?] (Achmite). *Kobell.*

35. $3BeO, 2Al^2O^3, 5SiO^2$ [?] (Euklase),—$3CaO, 2Al^2O^3, 5SiO^2$ [?] (Zoisite). *Brooke.*

One-and-one-membered or *Doubly Oblique Prismatic System.*

36. $MnO, SO^3, 4Aq$,—$MnO, SeO^3, 4Aq$,—$ZnO, SeO^3, 4Aq$,—$CoO, SeO^3, 4Aq$. *Mt.*

37. $CuO, SO^3, 5Aq$,—$CuO, SeO^3, 5Aq$,—$MnO, SO^3, 5Aq$. (*fig.* 121, 122, 123). *Mt.*

38. *a.* $NaO, 3CaO, 4Al^2O^3, 12SiO^2$ (Labrador).

b. $MgO, 3CaO, 4Al^2O^3, 8SiO^2$ (Anorthite).

Six-membered or *Rhombohedral System.*

39. $3AgS, AsS^3$ (Light red silver).—$3AgS, SbS^3$ (Dark red silver).

40. *a.* CaO, CO^2 (Calcspar),—MgO, CO^2,—$CaO, CO^2 + MgO, CO^2$,—MnO, CO^2,—ZnO, CO^2,—FeO, CO^2 (*fig.* 141 and *f.*)

b. NaO, NO^5,—KO, NO^5. *Frankenheim.*

41. *a.* SiO^2 (Quartz).—*b.* $CaO, Al^2O^3, 4SiO^2, 6Aq$. (Chabasite).

42. Al^2O^3 (Corundum),—Fe^2O^3,—Cr^2O^3,—$FeTiO^3$ (Ilmenite).

43. As,—Sb,—Te. *Breithaupt.* Tin also, according to Breithaupt, and zinc, according to Nöggerath, crystallize in regular six-sided prisms.

44. $SrO, S^2O^5, 4Aq$,—$CaO, S^2O^5, 4Aq$,—$PbO, S^2O^5, 4Aq$. *Heeren.*

45. $CaCl, 9CaO, 3PO^5$ (Apatite),—$PbCl, 9PbO, 3PO^5$ (Grünbleierz),—$PbCl, 9PbO, 3AsO^5$.

46. Mohsite and Eudialyte. *Brooke.*

47. *a.* Cd S,—Ni S,—Fe^8S^9.—*b.* Ni^2As (Kupfernickel),—Ni^3SbS^2 (Nickeliferous grey antimony).

c. Ir Os. *Breithaupt.*

48. H O and Zn O, crystallize in regular six-sided prisms, but their isomorphism has not yet been established by the determination of their angular relations.

From these data the isomorphism of the following simple and compound bodies may be deduced:

Carbon, phosphorus, potassium, titanium, bismuth, cadmium, lead, iron, copper, silver and gold? (1, *a*)

The isomorphism of iron and titanium is more completely established by (42) inasmuch as Fe^2O^3 and $FeTiO^3$ crystallize in the same form, and that of iron and cobalt by (25).

Potassium, sodium, lithium, calcium, zinc, lead, silver? (1, *b*)

Oxygen, sulphur, chlorine? (1, *c*)

Arsenic, antimony and tellurium (1, *d*, 13, 39, 43).

Platinum, iridium and osmium (1, *g*).

One atom of arsenic probably replaces two atoms of sulphur, inasmuch as Fe^2S^4 and Co^3AsS^2 have the same form (2); so likewise Fe^3S^4 and Fe^3AsS^2 (14).

Potassium and ammonium, NH^4 (1, *b* and *g*,—17, *b*).

K O and NH^4O; also under certain circumstances Na O (1, *h*,—5). On the other hand we might admit from (19) that $NH^4O + HO$ replaces K O.

Na O and Ag O (18, *a*). Just as K O in alum is isomorphous with Na O, so likewise in combination with NO^5 it may under peculiar circumstances crystallize in obtuse rhombohedrons exactly like those of NaO, NO^5 (41), so that NH^4O, K O, Na O, and Ag O, may be regarded as isomorphous in one or other of their states.

Mg O, Mn O, Zn O, Fe O, Co O, Ni O and [illegible] been shown to

be isomorphous in their combinations with carbonic, sulphuric and selenic acids (1, *e*,—4,—20,—22,—29,—30,—36). Lime, Ca O, is also related to them in one of its dimorphous states.

Pb O, Ba O, Sr O, and Ca O (in one of its states) are isomorphous (1, *f*,—3,—16,—17,—24,—44,—45).

According to (35), if the formulæ are correct, Be O is isomorphous with Ca O. According to (23), we might suppose that Na O is interchangeable with Ca O, H O.

Al^2O^3, Cr^2O^3 and Fe^2O^3, are isomorphous in the separate state (42); Mn^2O^3 is also isomorphous with them in combination (1, *e*,—1, *h*).

TiO^2 and SnO^2 are isomorphous in the separate state, (9) although Ti and Sn crystallize in different forms.

WO^3 in combination is isomorphous with MoO^3 and CrO^3 (3), also with TaO^3 (27).

SO^3 in combination is isomorphous with SeO^3, CrO^3, and MnO^3 (4,—7,—18, *a*,—19,—20,—26, *b*,—28,—29,—36,—37). CrO^3 seems also to form a connecting link of the series WO^3, MoO^3, CrO^3, MnO^3, SeO^3, and SO^3.

PO^5 and AsO^5 are also isomorphous in combination (5,—21,—32,—33,—35).

ClO^7 in combination is isomorphous with Mn^2O^7 (17, 6).

The following similarly formed compounds, however, differ so much in their chemical properties that their similarity of shape can scarcely be regarded as resulting from the substitution of one element for another:

Pb O, NO^3 and Pb O NO^5, (1, *f*) have the same form though they differ in composition by 2 At. oxygen.

Leucite and Analcime have the same composition, (1, *i*) excepting that the latter contains 2 atoms of water.

Copper-pyrites Cu FeS^2 and Braunite Mn^2O^3 (8). Here it must be supposed that 3 atoms of oxygen may be substituted for 2 atoms of sulphur.

Anatase and Apophyllite (10).—Zircon and Wernerite (11).—Manganite and Prehnite (15);—all differing irreconcilably in their chemical composition.

Arragonite, Ca O, CO^2 and nitre K O, NO^5 (16).*

Ba O, SO^3 on the one hand, and K O, ClO^7 and K O, 2Mn O^7 on the other (17).

Na O, SO^3 and Ba O, Mn^2O^7 (18).

SbS^5 and Mg O, SO^3, 7Aq (20).—S and K O, $2SO^3$, H O (26).—Borax, Na O, $2BO^3$, 10Ag and Augite, Cu O, Mg O, $2SiO^2$ (34).—Labrador and Anorthite (38).

Lastly, of totally dissimilar composition are: Ca O, CO^2 (Calcspar) and Na O, NO^5 (40).—Quartz and Chabasite (41).—Mohsite and Eudialyte.

Attempts have been made to bring some of these cases in accordance with the theory of isomorphism by altering the atomic weights of some of the substances concerned. The following is one of the most remarkable instances of this kind: Ca O, CO^2 as arragonite is isomorphous with nitre (K O, NO^5) in its usual form (16); Ca O, CO^2, as calcspar, with K O NO^5 as it is sometimes obtained, and with Na O, NO^5 as it always crystallizes. Hence Ca O, CO^2 in its two conditions is isomorphous with K O, NO^5 in its two conditions. For this reason Count Schaffgotsch halves the atomic weights of potassium and nitrogen; nitre then becomes $KO^{\frac{1}{2}}$, $NO^{2\frac{1}{2}} = KNO^3$. This agrees with Ca O, $CO^2 = Ca\,CO^3$;

in both compounds 3 atoms of oxygen are combined with 1 atom of metal and 1 atom of either carbon or nitrogen. This halving of the atomic weight of potassium involves the halving of those of ammonium (NH^4), sodium, silver and gold, because potash is isomorphous with oxide of ammonium (NH^4O) and soda, and the last of these with oxide of silver; and because silver in combination with the most various quantities of gold always crystallizes in the same form, a circumstance which indicates the isomorphism of these two metals. The halving of the atomic weight of silver had before been proposed by H. Rose, because in grey copper ore 1 atom of silver takes the place of 2 atoms of copper, and the crystalline form of AgS as well as that of Cu^2S belongs to the regular system. According to this view the atomic weights of N, H, K, Na, Ag, and Au would be reduced to one-half of the values now assigned to them; potash would be K^2O, soda Na^2O, oxide of silver Ag^2O, and suboxide of silver Ag^4O. By halving the atomic weights of potassium and chlorine the similar forms of KO, ClO^7 and BaO, SO^3 would also be explained, (17) for the composition would then be $KClO^4$ and $BaSO^4$.

Clarke, on the contrary, doubles the atomic weights of sodium and silver in order to reconcile the composition of NaO, SO^3 and AgO, SO^3 with that of BaO, Mn^2O^7 (18). He thus obtains NaO^2, $2SO^3 = NaS^2O^8$ and AgO^2, $2SO^3 = AgS^2O^8$; and this formula agrees with BaO, $Mn^2O^7 = BaMn^2O^8$. But since the atomic weight of potassium must be doubled as well as that of sodium, the explanation of case (18) becomes by this alteration more difficult than before.

With regard to these attempts, we cannot but agree with the view recently adopted by Johnstone (who formerly made trial of the same hypothesis as Count Schaffgotsch), viz. that many of the formulæ of isomorphous bodies cannot be made to agree with one another in any way whatever—others only by means of hypotheses which are either contradictory or greatly impair the simplicity of the chemical formulæ. Although similar formulæ often involve similarity of shape, it does not by any means follow that similar forms are inconsistent with dissimilar formulæ. There exists perhaps a higher law by which these cases might be explained: the discovery of such a law would give a new form to the theory of isomorphism.

Kopp and Schröder have remarked that isomorphous substances have equal atomic volumes (and therefore also equal atomic numbers). The simple substances (Table, page 55) exhibit approximations to this law, at least in some cases: *e.g.* Ni, Mn, Co and Fe; W and Mo; I, Br and Cl. But the atomic numbers of Sb and As, of Na and K, of Mn, Cr, S and Se, which at least are isomorphous in their acids, differ widely. According to table (page 68) equal atomic numbers are exhibited by Al^2O^3, Cr^2O^3 and Fe^2O^3; by TiO^2 and SnO^2; by WO^3 and MoO^3; by AsO^3 and SbO^3; by several anhydrous carbonates, sulphates and nitrates (some too not isomorphous); and by several hydrated sulphates. Exceptions are however presented by KO, SO^3 and KO, CrO^3; and by KCl, $NaCl$ and $AgCl$; moreover the merely approximate agreement in the atomic numbers of the first named compounds may in a great measure be explained by the fact that similar formulæ give nearly equal atomic weights, and these being used as divisors of nearly equal specific gravities, the quotients cannot differ much from another. On the other hand, Kopp has shown that the small differences between the angles at the edges of the obtuse rhombohedron of calcspar and the corresponding angles in the other carbonates which are isomorphous with it, probably bear a simple relation to the different volumes of the atoms of which these crystals are composed.

¶ A peculiar kind of isomorphism has recently been discovered by Scheerer (*Pogg.* 68, 319) which appears to play an important part in the mineral kingdom. By the analysis of a great number of minerals Scheerer finds that one atom of magnesia, protoxide of iron, or protoxide of manganese—and probably also of oxide of zinc, protoxide of nickel and protoxide of cobalt—may be replaced by 3 atoms of water, and one atom of oxide of copper by two atoms of water—without change of crystalline form.

This kind of isomorphism has received the name of *Polymeric Isomorphism:* it was first noticed in the minerals Cordierite and Aspasiolite. These two minerals crystallize in the same form, and crystals are found consisting partly of cordierite and partly of aspasiolite, the most complete transitions from one to the other occurring in the same specimen. Moreover, both minerals contain nearly the same proportions of silica and alumina; but aspasiolite contains a smaller quantity of magnesia and a larger quantity of water than condierite,—the difference being such that 3 atoms of water in the former may be regarded as the equivalent of 1 atom of magnesia in the latter. [*Vid.* Neumann, *Journ. für Prakt. Chem.* 40, 1.]¶

On the subject of Isomorphism see the already (page 32) cited treatises of Mitscherlich, Beudant, Wollaston, Hauy and Marx; likewise Kobell (*Schw.* 64, 41).—Breithaupt (*J. pr. Ch.* 4, 249 and *Pogg.* 51, 510). Persoz (*Ann. Chim. Phys.* 60, 119; also *Ann. Pharm.* 18, 241).—Brooke (*Phil. Mag. J.* 12, 406).—Johnston (*Phil. Mag. J.* 12, 235 and 480; 13, 305).—Count Franz Schaffgotsch (*Pogg.* 48, 335).

d. Relations to Heat.

Fusibility.—Compounds are, for the most part, more easily fusible than their elements. No metallic alloy is more refractory than either of its constituent metals, but many are more easily fusible than either of their components in the separate state. The earths also become more fusible by combination. An alloy of nickel and platinum melts at the same temperature as copper; alloys of lead and tin, lead and bismuth, &c., melt more easily than either of those metals by itself. Iron, by combining with the infusible substance, carbon (in steel and cast-iron), becomes more fusible than it is in the pure state. Silica is not fusible in the blast-furnace, neither is lime, baryta, strontia, alumina, or magnesia, —but the combinations of silica with these bodies are unable to resist such a temperature.

Many metallic sulphurets, on the contrary, are less fusible than their elements, *e. g.*, K S, Zn S, Sn S, Hg S; others are less fusible than sulphur, but more fusible than the metal, *e. g.*, Fe S, Ag S; but none of them are more fusible than sulphur.

Why the melting point of a compound should be sometimes between those of its elements, sometimes below, and sometimes, though rarely, above them both, has not yet been explained.

Volatility.—1. The elasticity of a compound is generally less than that of either of its elements. A solid or liquid may be formed by the combination of two gases, but no permanent gas is ever formed by the union of two liquid or solid bodies (p. 87). Phosphuret of nitrogen, when excluded from the air, will sustain a white heat without decomposition or volatilization, and even without fusion.

2. The volatility of a compound is very often of an intermediate degree; the more volatile element seems to impart a portion of its vola-

tility to the other. Carbon becomes gaseous by combining with oxygen, hydrogen, or nitrogen; sulphur with oxygen or hydrogen—selenium, iodine, bromine, arsenic, antimony, and phosphorus, with hydrogen; but all these gaseous compounds are less permanent than pure oxygen, hydrogen, or nitrogen gas, for most of them may be liquefied by pressure. Lead, silver, iron, &c., in combination with chlorine, are volatile at a moderate red heat.

3. Very few compounds are more volatile than either of their constituents. The most striking instance is that of sulphuret of carbon, which boils at 46° C. (= 114·8° Fah.)

These relations also have not yet been reduced to any regular law: thus much, however, may be said, that a compound of given elements is for the most part less volatile the greater the number of atoms of which the compound atom is made up. Sulphurous acid SO^2 is gaseous, sulphuric acid SO^3 is solid; the latter contains 1 atom more of the more volatile element, oxygen, but its total number of atoms is 4, that of sulphurous acid only 3. 1 At. nitrogen forms gaseous compounds with 1 and 2 At. oxygen, liquid compounds with 3 or 4 atoms of that element. Cyanogen, C^2N, is gaseous, mellon, C^3N^4, solid, although it contains a greater proportion of the more volatile element. In some cases, however, the greater volatility of one of the elements more than compensates for the greater number of atoms in the compound; thus Fe^2Cl^3 is more volatile than Fe Cl, though the former contains 5 atoms, the latter only two.

[For the specific heat of compounds *vide* Heat.]

e. Relations to Light.

Transparency.—A chemical compound is either transparent or opaque; in the former case it transmits light, coloured perhaps, but always clearly, because chemically combined bodies refract light as a whole; turbidity always indicates mechanical mixture. Two transparent substances always form a transparent compound, two opaque ones an opaque compound; the compounds of transparent with opaque bodies are sometimes opaque, sometimes transparent. Oxygen combined with metals sometimes forms transparent compounds, such as the alkalis and earths, oxide of zinc, oxide of antimony, arsenious acid; sometimes opaque compounds, *e. g.*, peroxide of manganese and magnetic iron ore: the compounds of sulphur with potassium, zinc, arsenic, and mercury are transparent, those with antimony, iron, copper, and silver, opaque. On the other hand, all the metallic fluorides, iodides, bromides, and chlorides appear to be transparent. According to this, fluorine, chlorine, bromine, and iodine would seem to have the greatest tendency to transparency, and oxygen a greater tendency than sulphur, inasmuch as the compounds of antimony, tellurium, and bismuth with oxygen are transparent, while their sulphurets are opaque. Among the metals those which show the smallest tendency to induce opacity in compounds, are the alkaline metals and arsenic; for all compounds of these metals with transparent substances are themselves transparent.

Refractive Power.—The refractive power of gaseous compounds is sometimes greater, sometimes less than the mean of the refractive powers of the constituent gases.

This is shown by the following table of Dulong (*Bullet. philomat.*, 1825, 132), which also contains the refractive powers of some of the simple gases. Column A contains the names of the gases;—B, their refractive powers determined by observation, that of air = 1;—C, the

active power which the compound gases should exhibit according to calculation, taking the mean between the refractive powers of the component gases;—D, their specific gravities;—E, the specific refractive power, obtained by dividing the observed refractive power by the specific gravity.

A.	B.	C.	D.	E.
Air	1·000		1·0000	
Oxygen	0·924		1·1093	0·83
Hydrogen	0·470		0·0693	6·79
Chlorine	2·623		2·1543	1·06
Nitrogen	1·020		0·9706	1·05
Carbonic oxide	1·157		0·9709	1·21
Carbonic acid	1·526		1·5252	1·00
Sulphurous acid	2·260	1·619	2·2185	1·02
Sulphuretted hydrogen	2·187		1·1786	1·85
Vapour of sulphuret of carbon	5·179		2·6345	1·97
Hydrochloric acid gas	1·527	1·547	1·2618	1·21
Phosgene gas	3·936	3·784	3·4249	1·15
Nitrous oxide	1·710	1·482	1·5252	1·12
Nitric oxide	1·030	0·972	1·0399	0·99
Ammoniacal gas	1·309	1·216	0·5893	2·22
Olefiant gas	2·302		0·9706	2·36
Light carburetted hydrogen	1·504		0·5546	2·71
Cyanogen	2·832		1·8026	1·57
Hydrocyanic acid vapour	1·531	1·651	0·9359	1·63
Alcohol vapour	2·220		1·5946	1·39
Ether vapour	5·280		2·5652	2·05
Vapour of hydrochloric ether	3·720	3·829	2·2322	1·67

From these numbers Dulong concludes that when a compound gas is of an acid nature its refractive power is below the calculated mean, but above the mean when the gas is alkaline or neutral; hydrochloric ether, however, forms an exception to this rule. If it be admitted that the refractive power of a substance is directly proportional to its density and inflammability, the latter will be found by dividing the refractive power by the specific gravity. The quotients in column E agree very well with this view; hydrogen has the greatest refractive power, and oxygen, the substance most opposed in its properties to combustible bodies, the smallest. The other numbers also agree, excepting that the refractive power of sulphuret of carbon should be smaller than that of sulphuretted hydrogen, since the former contains 2 atoms of the less combustible substance sulphur to 1 atom of carbon, the latter equal numbers of atoms of sulphur and hydrogen; the refractive power of nitrous oxide, again, ought to be smaller than that of nitrogen, since nitrogen must lose some of its refracting power by combining with oxygen.

Some compounds, in passing from the gaseous to the liquid state, increase in refracting power more than in density, as was first noticed by Arago and Petit. The absolute refractive power of liquid sulphurous acid ought, according to calculation from that of the gas to be 0·661: its actual value, however, is, according to De la Rive, 0·78 (*Ann. Chim. Phys.* 40, 410, *extr. Pogg.* 15, 528); that of liquid ammonia should by calculation from that of ammoniacal gas be 0·725, and that of sulphuretted hydrogen 0·767; but according to Faraday, the refractive powers of both these liquids exceed that of water, which is 0·784.

Colour.—Colourless substances generally produce colourless compounds; but colourless nitrogen combined with colourless oxygen forms blue nitrous acid and red hyponitric acid; and in the organic kingdom we see a great variety of coloured compounds formed by the union of carbon (which is colourless, at least in the diamond), hydrogen, oxygen, and sometimes also nitrogen. Coloured bodies, such as sulphur, selenium, iodine, and the metals generally form coloured compounds by combination amongst themselves; nevertheless, iodide of potassium, chloride of lead, and chloride of silver, &c. are colourless. The compounds of coloured with colourless bodies are sometimes coloured, sometimes not; thus the compounds of oxygen with sulphur, selenium, iodine, bromine, chlorine, and most of the lighter metals, are white, those with the heavier metals coloured. In the present state of chemical knowledge the colour of a compound cannot be determined beforehand from those of its constituents; it often differs greatly from them. The red metal copper combined with colourless oxygen forms a brown-black oxide, and this combined with colourless sulphuric acid forms a white salt, which again in combination with water produces the blue crystals of hydrated sulphate of copper or blue vitriol. Grey chromium with a certain quantity of oxygen forms a green oxide, which, combined with various colourless acids, forms salts of which some are green, some violet; with a larger quantity of oxygen chromium forms the yellowish red chromic acid, whose compounds with bases are sometimes yellow sometimes red.

The law of Persoz, (*Ann. Chim. Phys.* 60, 127; also *Ann. Pharm.* 18, 256), viz. that when the higher oxide of a metal is white or slightly coloured, the lower is blue or dark coloured, and when the higher oxide has a dark colour, the lower is white or faintly coloured, is true as regards cerium, titanium, tantalum, tungsten, molybdenum, and manganese, but not with regard to arsenic, antimony, and tellurium, both whose oxides are white or light-coloured, nor with regard to copper, silver, gold, platinum, and others, both whose oxides are dark-coloured.

f. Chemical and Physiological Relations.

A chemical compound generally differs altogether from its elements, both in its affinities and in its action on living animal bodies. In some cases, combination develops active chemical and physiological properties, in others it destroys those which previously belonged to the elements.

Neither sulphur nor oxygen exhibits any affinity for the greater number of salifiable bases; but the affinity of sulphuric acid for these bases is very strong: again, neither of these elements reddens the blue colour of litmus, but this effect is readily produced by sulphuric acid; the same elements are also tasteless and destitute of corrosive action, whereas sulphuric acid has a sour taste and is highly corrosive. Nitrogen, again, which by itself is one of the most indifferent of the elements, produces in combination with oxygen the corrosive substance nitric acid, with hydrogen the powerful alkali ammonia, and with carbon and hydrogen the highly narcotic hydrocyanic acid. The poisonous action of many metals is not developed till they are combined with oxygen, chlorine, or other bodies of like nature. Are these properties actually produced by the act of combination, or are they previously latent in the elements and brought into active operation when those elements are combined with others?

Persoz (*Ann. Chim. Phys.* 60, 127, also *Ann. Pharm.* 18, 255) has laid down the two following laws:—1. All bodies which in combination with chlorine form compounds volatile below the boiling point of mercury,

duce acids when combined with oxygen; viz. hydrogen [?], carbon, ron, phosphorus, sulphur, selenium, bromine, iodine, nitrogen, silicium, tanium, tungsten, vanadium, chromium, uranium, manganese, arsenic, antimony, tin, and osmium. This law appears to fail in the case of mercury itself, which produces no acid, but is notwithstanding less volatile than corrosive sublimate. 2. All compounds containing 1, 3, 5 or 7 atoms of oxygen are either acid or basic; those on the contrary which contain 2 or 4 atoms of oxygen are, with a few exceptions which disappear on a particular hypothesis, neither acid nor basic. Exceptions to this law are—C O, which is neither acid nor basic, Mo O^2, V O^2, and Pt O^2, which are bases, and C O^2, S O^2, Se O^2, Ti O^2, Sn O^2, and Te O^2, which are acids. The manner in which Persoz endeavours to get rid of these exceptions looks like a gratuitous assumption. It is nevertheless true that by far the greater number of acids and bases contain an uneven number of atoms of oxygen.

The case in which marked chemical and physiological properties existing in elements are caused to disappear by combination is most strikingly exhibited in the combination of acids with salifiable bases: the effect is then called *Neutralization*. When an acid and a base combine in certain proportions, their opposite properties are mutually destroyed, and a more or less indifferent compound is the result. Hydrochloric acid, for example, tastes and smells strongly acid and reddens litmus; ammonia has a powerful alkaline smell and taste, restores the blue colour of litmus which has been reddened by an acid, reddens turmeric, and gives a green colour to violet juice—these changes of colour being again removable by acids; both these substances in the concentrated state exert a powerful caustic action on the animal body though in different ways, and cannot therefore be swallowed without injury, except in very small quantities and in a state of dilution. If now the aqueous solution of hydrochloric acid and aqueous solution of ammonia, be mixed in certain proportions (the required proportions may be ascertained by the use of litmus or turmeric paper), a perfectly neutral compound will be obtained, which reddens neither litmus nor turmeric, tastes and smells neither acid nor alkaline, but is devoid of smell and has a saline taste, has no corrosive action, and may be swallowed in much larger quantities. The two substances have therefore *neutralized* each other both chemically and physiologically; a *neutral compound* has been formed; *neutrality*, chemical equilibrium, chemical indifference has been produced. The proportion in which this mutual destruction of chemical properties is most completely effected is called the *point of neutralization*. Exactly one atom of hydrochloric acid is required to neutralize one atom of ammonia. If to this neutral compound a fresh quantity of hydrochloric acid be added, the character of the acid will again become evident by its sour taste and its effect on litmus; it will *prevail, preponderate*, or be *in excess*, or the ammonia will be *supersaturated* with hydrochloric acid: similar results, only of the opposite character, would be obtained by adding more ammonia to the neutral compound.

Addenda to the Theory of the Qualitative Alteration of Elements in Combination.

Although the properties of a compound are mainly dependent on those of its elements, and on the proportion in which these elements are combined, it has nevertheless been shown by recent experiments that other

circumstances likewise have an influence on this matter, and that compounds may exist composed of the same substances in the same proportions, and yet possessing very different properties. To this part of the subject belong Mitscherlich's theory of Dimorphism, Fuchs's theory of Amorphism, and Berzelius's theory of Isomerism, Polymerism, and Metamerism.

a. Differences in the Properties of Compounds, which may be explained on the Hypothesis of different Modes of Arrangement of their Compound Atoms.

α. Dimorphism and Trimorphism.

The same substances, whether simple or compound, may crystallize in forms which belong to two or three different systems of crystallization, or which, even if they belong to the same system, yet exhibit such differences in their corresponding angles as to render it quite impossible to reduce them to the same form: this was first shown by Mitscherlich. This difference of crystalline form is associated with difference of specific gravity, hardness, colour, and other properties. Whether a body shall crystallize in one system or another seems to depend chiefly on temperature. Crystals formed at one particular temperature, and then exposed to that temperature at which crystals of a different kind are produced, often lose their transparency, and, without alteration of external form, become changed into an aggregate of small crystals of the latter kind. We may therefore imagine that the atoms of the solid crystal displace one another in such a manner as to bring about that particular arrangement which they are disposed to assume at the altered temperature, the new arrangement belonging to a different crystalline system.

The cases of Dimorphism hitherto observed, including those relating to simple substances, are as follows:—

Carbon in the diamond forms crystals belonging to the regular system, in graphite to the rhombohedral system,—unless the latter are to be regarded as pseudomorphous crystals.

Sulphur crystallizes, on cooling from a state of solution in sulphuret of carbon, in rhombic octohedrons belonging to the right prismatic system (*fig.* 41—44), exactly like those of native sulphur; if, on the other hand, melted sulphur be allowed to cool slowly till a portion of it has become solid, and the still liquid portion be then poured out, the solidified portion exhibits oblique rhombic prisms belonging to the oblique prismatic system. These are at first perfectly transparent, of a deep yellow colour, and somewhat harder and denser than those of sulphur crystallized in the cold; but after being kept for a few days at ordinary temperatures, they become opaque, and of a straw-yellow colour. At the lower temperature, therefore, the atoms of sulphur arrange themselves in such a manner as to form a rhombic octohedron, at the higher temperature just below the melting point (about 107° C., or 224° Fah.), the mode of arrangement is such as to produce an oblique rhombic prism. When these last-mentioned crystals are brought to a lower temperature, a general displacement of the atoms appears to take place, whereby they are brought into the particular relative position which belongs to the rhombic octohedron; and this change destroys their transparency, because in place of one crystal an aggregate of crystalline particles is produced which refract light in different directions (Mitscherlich). According to Frankenheim (*J. pr. Chem.* 16, 5), sulphur assumes the form of the

ne rhombic prism when precipitated from solutions or sublimed at peratures near its melting point.

Native copper generally occurs in cubes and other forms belonging to he regular system; but Hauy once found it in double six-sided pyramids with truncated edges (*fig.* 138). Seebeck likewise obtained copper after fusion in crystals belonging to the rhombohedral system. According to Haidinger and H. Rose (*Pogg.* 23, 197), however, these crystals, which appear to belong to the rhombohedral, are really macle crystals of the cube with pyramidal summits (*fig.* 9), and therefore belong likewise to the regular system.

Suboxide of copper occurs in ordinary red copper ore in regular octohedrons and other forms belonging to the regular system, but in copper-bloom it exhibits a regular six-sided prism, whose planes of cleavage are parallel to the faces of an obtuse rhombohedron. (Succow, *Pogg.* 34, 528.) This may be regarded as a case of dimorphism similar to that of copper, insofar as the latter is really dimorphous.

Protoxide of lead crystallizes after fusion, as well as from a saturated solution in hot concentrated caustic potash, in yellow rhombic octohedrons. If, however, the solution is not fully saturated with oxide of lead, so that crystallization does not take place till after complete cooling, red crystalline scales are deposited on the yellow rhombic octohedrons just formed: if the red crystals are heated they turn yellow on cooling, in consequence of passing into the first form. (Mitscherlich, *J. pr. Chem.*, 19, 451.)

Oxide of titanium, $Ti O^2$, occurs in nature in the two forms of anatase and rutile. Although both these crystals belong to the square prismatic system, their angles are incompatible; they cannot be reduced to the same primitive form; the specific gravity also of anatase is 3·826, that of rutile 4·249.

Arsenious acid, $As O^3$, generally crystallizes in regular octohedrons; but Wöhler (*Pogg.* 26, 177) found it also in the form of native oxide of antimony, $Sb O^3$ (Weissspiessglanzerz), which belongs to the right prismatic system. Wöhler also obtained artificially crystallized oxide of antimony in regular octohedrons. Consequently $As O^3$ and $Sb O^3$ are *iso-dimorphous; i. e.*, they are capable of crystallizing in two different forms which are similar each to each.

Disulphuret of copper, $Cu^2 S$, appears in copper glance in crystals of the rhombohedral system (*fig.* 131, 132, 135, 137); but Mitscherlich (*Pogg.* 28, 157), by melting together large quantities of copper and sulphur, obtained it in regular octohedrons. These two forms are the same as those of copper and its red oxide.

Bisulphuret of iron occurs in nature as iron pyrites in crystals belonging to the regular system, (*fig.* 18, 19, 20,) and as white iron pyrites in those of the right prismatic system, the latter being of a paler yellow and much softer. Breithaupt imagines that the oblique rhombic sulphur which may be supposed to exist in common iron pyrites, has imparted the hemihedral character to the iron which has retained its original system, —and that the white pyrites, which in form resembles the rhombo-octohedral sulphur, may contain this kind of sulphur; and, accordingly, that the white pyrites has been formed at a lower temperature than the common variety.

Protiodide of mercury separates from solution, and likewise sublimes at a very gentle heat in scarlet tables belonging to the square prismatic system, but when sublimed at a higher temperature, in sulphur-yellow rhombic tables of the oblique prismatic system. The red crystals turn

yellow as often as they are heated, and resume their red tint on cooling. The yellow crystals obtained by sublimation retain their colour when cooled; but on the slightest rubbing or stirring with a pointed instrument, the part which is touched turns scarlet, and this change of colour extends, with a slight motion, as if the mass were alive, throughout the whole group of crystals as far as they adhere together. In this case the yellow crystals retain their external form unchanged, while the compound atoms must have taken up the relative position which belongs to the red crystals; the yellow crystals are therefore pseudomorphous. The same crystals turn yellow every time they are heated, and red again on cooling. (Hayes, *Sill. Am. J.*, 16, 174; also *Schw.*, 57, 199.) The original red crystals also turn yellow when heated, and retain this colour after cooling for several days, even when touched with foreign bodies, and at length spontaneously, but very slowly, resume their red colour. When the red crystals are sublimed at a very gentle heat, red and yellow crystals sublime together. If a glass plate, having both red and yellow crystals on it, be warmed so gently that the red ones do not change colour, but sublimation nevertheless goes on, both red and yellow crystals collect on a plate held above the former. Now, since the upper plate is cooler than the lower, and the latter is not hot enough to change the colour of the red crystals, the yellow crystals on the upper plate can have come only from those of the same colour on the lower; they must, therefore, have sublimed as yellow crystals, and the vapour of the yellow crystals must be different from that of the red ones. (Frankenheim, *J. pr. Chem.*, 16, 4.)

Carbonate of lime, CaO, CO^2, in the form of calcspar, whose sp. gr. = 2·721, belongs to the rhombohedral, in arragonite, whose sp. gr. is 2·931, to the right prismatic system. (An explanation of this difference was formerly sought in the fact discovered by Stromeyer, viz., that arragonite usually contains small quantities of carbonate of strontia.) The same peculiarity is presented by carbonate of iron, FeO, CO^2, which in sparry iron ore (of 3·872 sp. gr.) has the form of calcspar, in junkerite (of 3·815 sp. gr.) that of arragonite. Hence Ca, Co^2, and FeO, CO^2 are isodimorphous. If a solution of carbonate of lime in water containing carbonic acid be left to evaporate at the ordinary temperature, nothing is obtained but calcspar, in microscopical and for the most part truncated primitive rhomboids (*fig.* 142); if, on the contrary, the solution be evaporated over the water-bath, arragonite is obtained in small 6-sided prisms, mixed with a few crystals of calcspar, because the temperature of the solution is lower at first than it afterwards becomes, and the sp. gr. of the liquid is not higher than 2·803. When an aqueous solution of chloride of calcium is mixed at ordinary temperatures with an aqueous solution of carbonate of ammonia, a voluminous flocculent precipitate of chalky (amorphous?) carbonate of lime is first produced, which if immediately collected on a filter, washed and dried, remains unaltered, possessing a sp. gr. of 2·716, and appearing under the microscope to consist of small opaque granules; but if this same precipitate be left for some time in the saline liquid from which it has been precipitated, it collects into microscopical crystals of calcspar, of 2·719 sp. gr. If the same saline solutions be mixed boiling, the carbonate of ammonia being added to the chloride of calcium, arragonite is obtained, mixed with a small portion of calcspar. If, on the contrary, the chloride of calcium be added to the carbonate of ammonia, arragonite is obtained alone, in exceedingly small crystals of 2·949 sp. gr. If, however, these crystals are not immediately collected

on a filter, washed and dried, but allowed to remain in the liquid, they gradually change after the liquid has cooled, and in about a week are completely converted into calcspar; in pure water this transformation goes on much more slowly. When carbonate of lime is fused under strong pressure, as in Hall's method, it invariably crystallizes on cooling in the form of calcspar. A tolerably large crystal of arragonite falls to pieces at a low red heat without losing weight, and forms a white opaque coarse powder, having a sp. gr. of only 2·706. Hence it follows that carbonate of lime crystallizes at about 100° C. in the form of arragonite, but at a lower temperature, or at a red heat, in the form of calcspar. The arragonite which occurs in the caverns of volcanic districts must have been formed by infiltration while the mass was yet warm. According to these experiments, carbonate of strontia is not necessary to the formation of arragonite; indeed, many specimens of natural arragonite are free from it. Since, however, arragonite and carbonate of strontia crystallize in the same form, the latter may often become mixed with crystals of the former. If chloride of strontium be decomposed by carbonate of ammonia in the cold, carbonate of strontia precipitates in an indeterminate form, but assumes the form of arragonite on being heated. Chloride of barium and chloride of lead, treated with carbonate of ammonia in the cold, yield precipitates of carbonate of baryta and carbonate of lead in the form of arragonite. The carbonates of baryta, strontia, and lead, cannot be made to assume the form of calcspar. (H. Rose, *Pogg.*, 47, 353.)

Nitrate of potash usually crystallizes in prisms of the form of arragonite: but if a drop of the aqueous solution of this salt be left to evaporate on a glass plate and the crystallization observed under the microscope, it will be found that side by side with the prismatic crystals at the edges of the drop, a number of obtuse rhomboids of the calcspar form are produced just like those in which nitrate of soda crystallizes. As the two kinds of crystals increase in size and approach one another, the rhomboids become rounded off and dissolve, because they are more easily soluble than the others, while the arragonite-shaped prisms go on increasing in size. When the two kinds of crystals come into immediate contact, the rhomboidal ones instantly become turbid, acquire an uneven surface, and after a short time throw out prisms from all parts of their surfaces. Contact with foreign bodies also brings about the transformation of the rhomboids while they are wet. If the drops are so shallow that the liquid dries round the rhomboids before they are disturbed, they will remain for weeks without disintegrating, and bear gentle pressure with foreign bodies without alteration; but stronger pressure, or scratching, or the mere contact of a prismatic crystal of saltpetre causes them to change, a delicate film proceeding, as it were, from the point of contact and spreading itself over their surfaces; they then behave towards foreign bodies like a heap of fine dust, but retain their transparency. The rhombohedrons are also transformed without alteration of external appearance when heated considerably above 100° C.: they then become much harder, because the fine powder first produced bakes together into prismatic crystals. A hot solution of saltpetre yields when slightly cooled nothing but prismatic crystals; but at 10° C., (+ 14° Fah.) prismatic and rhombic crystals appear together; if alcohol be added, the latter are formed most abundantly; the addition of potash, nitric acid or nitrate of soda produces no alteration. (Frankenheim, *Pogg.* 40, 447; also *J. pr. Chem.* 16, 1.)

Sal-ammoniac which commonly crystallizes in regular octohedrons

appears at higher temperatures to assume forms belonging to the right prismatic system. (Frankenheim, *J. pr. Chem.* 16, 3.)

Iodide of potassium, which usually crystallizes in cubes, likewise forms square prisms with truncated summits (*fig.* 32) which cannot be regarded as cubo-octohedrons because their *e*-faces make an angle of 120° with *p* and of about 150° with *q*. (Kane, *Phil. Mag. J.* 16, 222.)

Chromate of lead occurs in red lead spar in the form of oblique rhombic prisms: but in chromate of lead from the Banuat the same substance presents forms belonging to the square prismatic system, having the same angles as molybdate of lead. (Johnston, *Phil. Mag. J.* 12, 387.)

Sulphate of nickel (Ni O, SO^3, 7Aq) crystallizes (*a*) below 15° C. (59° Fah.) in right rhombic prisms (*fig.* 73); (*b*) between 15° and 20° C. (59° and 68° Fah.) in acute octohedrons with square bases (*fig.* 36, 37); and (*c*) above 30° C. (86° Fah.) in oblique rhombic prisms, also in forms belonging to the right, square, and oblique prismatic systems: it is therefore *trimorphous*. The right rhombic prisms (*a*) when exposed to sunlight for a few days, neither liquefy nor lose their form or water of crystallization, but when broken are found to be made up of square-based octohedrons often several lines in length.

The following salts isomorphous with sulphate of nickel have hitherto been obtained in only two out of the three forms just mentioned. Sulphate of zinc (Zn O, SO^3, 7Aq) crystallizes below 52° C. (125·6° Fah.); in form *a*, below 52° C., as observed by Haidingen in less transparent crystals like *c*; if crystal *a* be heated in oil or in a glass tube above 52° C, it becomes soft at certain points without losing water excepting any that may be adhering to it mechanically, and from these points bundles of milk-white crystals *c* shoot out towards the inside of the transparent crystal until the whole is completely transformed. If the crystals obtained above 52° be slowly cooled after drying they remain tolerably clear; but when cooled quickly before drying they become opaque, and when broken are often found to consist of an aggregate of crystals *a*, these having been first formed in the adhering mother-liquid and subsequently extended through the crystals already formed. Sulphate of magnesia (Mg O, SO^3, 7Aq) like sulphate of zinc, yields right rhombic prisms *a* below 52°, and oblique rhombic prisms *c* above 52°; and the crystals *a* when heated above 52° are immediately converted into an opaque aggregate of crystals *c*, which proceed from the surface of the crystals and meet in the middle. Seleniate of zinc (Zn O, $Se O^3$, 7Aq) crystallizes at a lower temperature like *a*, at a higher temperature like *b*, and the crystals *a* undergo an alteration of internal structure when exposed to sunshine. (Mitscherlich, *Pogg.* 6, 19 and 12, 144.)

Acid phosphate of soda (Na O, PO^5, 4Aq) crystallizes in two series of forms (*fig.* 61—64) both of which belong to the right prismatic system but have incompatible angles. (Mitscherlich.)

Vesuvian (*fig* 39) and garnet (*fig.* 3) consist of the same chemical compound, crystallized in forms which belong to the square prismatic and regular systems respectively (*Comp.* page 106).

Karsten likewise regards as dimorphous compounds: Augite and tabular spar; felspar and albite; sodalite and scapolite.

β. Amorphism.

Every solid body is either crystalline or amorphous. In the latter state it is destitute not only of crystalline form but of all traces of crys-

talline structure even in its smallest particles. It has no power of double refraction as many crystals have, no planes of cleavage, being equally easy or equally difficult of separation in all directions, and exhibits when broken not a granular but a conchoidal fracture. Marble and even common limestone are not amorphous bodies but aggregates of small, imperfectly developed crystals: glass is amorphous.

We often find the same body assuming the crystalline or the amorphous condition according to the circumstances under which it passes from the liquid to the solid state: some bodies again are more inclined to the crystalline, others to the amorphous state: some are known to exist in one only of these conditions. The same body is generally speaking specifically heavier, harder, and less soluble in the crystalline than it is in the amorphous state: the atoms seem to be more closely packed in the former condition than in the latter. According to Graham, an amorphous body also contains a larger quantity of combined heat than one which has a crystalline structure. The passage of a body from the amorphous to the crystalline state is called by Fuchs *Transformation*, and the change from the crystalline to the amorphous state *Deformation*. The amorphous state is particularly apt to occur when the atoms, either from viscosity in the liquid or a too rapid passage from the liquid to the solid state, are not able to arrange themselves in that peculiar manner which constitutes crystalline structure.

An amorphous body may be produced:—

1. By fusion—the process is then called *Vitrification*.—Common glass, many slags, obsidian, pumice-stone, pearl-stone, vitrified borax, phosphoric acid, arsenious acid, arsenic acid, boracic acid, &c. All bodies which solidify in the amorphous state form viscid liquids when melted. If a body appears transparent immediately after cooling from a state of fusion it may generally be regarded as amorphous; but if it becomes opaque upon cooling, although it was transparent while melted, it is then most probably crystalline, (*e.g.* hydrate of potash and carbonate of lime): because the numerous small crystals interlacing each other in all directions refract light in a confused and irregular manner. According to Graham, acid phosphate of soda gives out less heat at the moment of solidification than acid arseniate of soda; the former solidifies in the form of a transparent glass; the latter in that of an opaque fibrous mass.

2. By evaporation of a solution.—A solution of gum, glue, white of egg, soluble glass, &c. in water, and of most resins in alcohol, leaves the dissolved bodies in an amorphous state when the liquid evaporates. All these bodies require but a very small quantity of the solvent to retain them in the liquid state: consequently, after the greater portion of it has evaporated, they still remain dissolved and form very thick solutions, the viscosity of which appears to prevent the particular mode of approximation of the atoms required for crystallization.

3. By precipitation.—Most if not all voluminous, gelatinous, and viscid precipitates must be regarded as amorphous. Some of them retain this condition even after remaining for a long time in the liquid, and form, after washing and drying, earthy or transparent masses having a conchoidal fracture like alumina or phosphate of lime; others sink to the bottom of the liquid in which they are produced, and with various degrees of rapidity collect themselves into an aggregate of small crystals, *e.g.* uric acid and carbonate of lime. [*Comp.* Link (*Pogg.* 46, 258); Mitscherlich (*Ann. Chim. Phys.* 73, 389); Erdmann (*J. pr. Chem.* 19, 343, 345 and 353.)]

The following is a list of bodies, elementary substances included, in which both conditions have been observed:

Carbon is crystallized in the diamond, amorphous in charcoal and lamp-black, and according to Fuchs's view in graphite also.

Phosphorus kept under water in the dark becomes covered with a white opaque crust which contains no water but consists of pure phosphorus, and when heated above 104° Fah. melts again without loss of weight to the state of ordinary phosphorus. (H. Rose, *Pogg.* 27, 563.) One of these two conditions is probably amorphous.

When sulphur is heated considerably above its melting point to about 180° or 200° C. (356° or 390° Fah.) till it becomes quite viscid and then poured into water, it solidifies to a soft hyacinth-red vitreous mass, which however in a few days resumes its crystalline structure and becomes yellow and opaque. (Fuchs.) When this soft vitreous sulphur is placed in an oven heated to about 98° C. (208° Fah.) its temperature as soon as it reaches 93° C. (199·4° Fah.) rises suddenly to 110° C. or 230° Fah. and it then becomes hard: consequently, at a temperature near its melting point the sulphur passes quickly to its ordinary crystalline state, the change being accompanied by a disengagement of heat. (Regnault, *Ann. Chem Phys.* 76, 206.) At different temperatures melted sulphur may exist in three different states, colourless, yellow and red. By warming a small quantity of flowers of sulphur on a glass plate, or by sublimation, we may obtain colourless drops which often remain for weeks without crystallizing: they appear to correspond to the rhombo-octohedral sulphur. At a higher temperature these drops become yellow, then by a quick transition green, and lastly dark red. A drop of sulphur unequally heated exhibits a sharp demarcation of the red and yellow portions; the crystals first formed by cooling do not extend into the red part. The yellow melted sulphur may perhaps correspond to the oblique rhombic, the red to some other (the amorphous) variety. (Frankenheim, *J. pr. Chem.* 16, 5.)

Silicium which has not been ignited burns when heated in the air: but that which has been previously ignited in hydrogen gas does not: the former is probably amorphous, the latter crystalline and therefore more coherent.

The remarkable properties of platinum-black are in all probability due to an amorphous condition of the metal.

The grey native sulphuret of antimony and the brown-red substance called Kermes mineral, must be regarded as the same compound $Sb S^3$ in its crystalline and amorphous states. Kermes mineral fused out of contact of air suffers no alteration in weight, but crystallizes on cooling into a mass resembling the native sulphuret: on the other hand, Fuchs has shown that when the latter is kept in the fused state for a considerable time in a narrow glass tube (if fused for a short time only the alteration is not complete) and then thrown into cold water, a shining dark grey mass is obtained, which appears of a dark hyacinth-red colour by transmitted light when in thin films, has a conchoidal fracture and a sp. gr. of 4·15, while that of the native sulphuret is 4·752; when rubbed it yields a red-brown powder similar to Kermes mineral, but somewhat darker; whereas the native sulphuret, however finely it may be powdered, retains its grey colour. When this quickly cooled mass is again melted and suffered to cool slowly, it returns to the crystalline state of the native sulphuret. Rapid cooling prevents the crystalline arrangement, and the body remains for the most part amorphous.

The black sulphuret of mercury obtained by treating a protosalt of mercury with excess of sulphuretted hydrogen has exactly the same composition as cinnabar, viz., Hg S, and when sublimed passes without alteration of weight to the condition of that substance: on the contrary, according to Fuchs, when finely pounded cinnabar is heated till it begins to sublime, and then thrown into cold water, it is converted into the black sulphuret. In this case, contrary to that of sulphuret of antimony, the crystalline sulphuret is red and transparent, whilst the amorphous variety is grey and opaque.

Chromate of lead, when slowly cooled from a state of fusion, is brown and yields a yellowish brown powder, but when suddenly cooled by throwing it into cold water, it is red, and yields a red powder. (Marchand, *J. pr. Chem.* 19, 65.)

Quartz has a specific gravity of 2·652, refracts light doubly, is but very slightly soluble in boiling solution of potash, and does not harden, however finely it may be divided, in contact with lime and water. Opal has a sp. gr. of 2·09, refracts singly, dissolves easily in boiling caustic potash, slowly in the same when cold, and hardens with lime and water into a mortar. Both minerals consist of silica. Opal, however, contains from 3 to 12 per cent. of water, and the difference between them has been ascribed to this circumstance, opal being regarded as a hydrate of silica. But for this the quantity of water in opal is too small and too variable. Fuchs, therefore, regards opal as amorphous silica, and his view is supported by the fact that opal, after all its water has been driven off by ignition, presents almost the same appearance and is nearly as soluble in potash as before. Silica, artificially prepared (by fusing any siliceous mineral with potash, treating the fused mass with dilute hydrochloric acid in excess, evaporating to dryness, and digesting in water,) has likewise, after ignition, the same action with caustic potash that opal has, and must therefore in like manner be regarded as amorphous. Chalcedony is a mixture of quartz and opal; boiling caustic potash dissolves out the latter and leaves the former in the state of cachelong.

Arsenious acid, when sublimed on the large scale, solidifies from the effect of the high temperature into a perfectly transparent glass. This white glass, when kept at ordinary temperature for several months, becomes turbid and subsequently white and opaque. In this case there is probably a transition from the amorphous to the crystalline state; but it is remarkable that (according to Guibourt) the specific gravity diminishes from 3·785 to 3·695, and that the opaque acid dissolves rather more abundantly both in hot and in cold water than the transparent, whereas in other cases the change from the amorphous to the crystalline state is accompanied by increased density and diminished solubility. When the transparent acid is dissolved in boiling dilute hydrochloric acid and the solution left to cool slowly, every crystal as it separates emits a vivid light. The opaque acid, when similarly treated, exhibits no phosphorescence, unless it contains some of the transparent acid mixed with it. It appears then that the transition from the amorphous to the crystalline state, which takes place when the acid crystallizes from its solution in hydrochloric acid, is accompanied by an emission of light. (H. Rose, *Pogg.* 35, 481.) This phenomenon seems also to show that even in a state of solution the atoms of a solid may be arranged, sometimes in the amorphous, sometimes in the crystalline order; in the present instance, since the solution of the transparent acid emits light on crystallizing and

that of the opaque acid does not, the former must contain the acid in the amorphous state.

Green glass, kept for several hours or for days at a red heat, just trong enough to soften it, acquires a fibrous texture, the change proceeding gradually from the surface towards the interior, and is finally converted into the substance called Reaumur's porcelain, which is white, slightly transparent, mostly of fibrous fracture, specifically heavier, less fusible, and much harder than the glass out of which it has been formed. This change, which takes place without loss of weight, may be attributed to a crystalline arrangement of the atoms brought about by keeping the glass for a long time in a soft state. (*Vid.* Silicium.)

Basalt, which is an aggregate of crystalline granules, is converted by fusion into a black glass; and this when kept for a long time at a red heat becomes once more fine-grained and opaque.

A mixture of clay, lime, and magnetic iron ore, yielded when intensely heated a black slag; this, after it had solidified and nearly cooled, suddenly became red hot, and fell to pieces in the state of a fine grey powder. (Fuchs)

Sugar which has been melted, as in barley-sugar and bonbons, is in a vitreous condition, but after some time becomes white and opaque. If melted sugar is allowed to cool to about 38° C. or 100 Fah., and then, while it is yet soft and viscid, rapidly and frequently extended and doubled up, till at last it consists of threads, its temperature rises in two minutes from 104° to 176° Fah., and it then consists of minute crystalline grains of a pearly lustre. (Graham, *Elements of Chemistry*, page 43.)

Vesuvian and calcareous garnet (grossularia) have the same composition: for example, the Vesuvian, and garnet from the Wiluifluss have the same formula, $3CaO, Al^2O^3, 3SiO^2$, excepting that in both minerals part of the alumina is replaced by peroxide of iron which is isomorphous with it. Vesuvian, which crystallizes in square prisms, has a specific gravity of 3·4; garnet, which crystallizes in rhombic dodecahedrons, a specific gravity of 3·63. These dimorphous minerals both pass by fusion into the amorphous state; they both, when subjected to this treatment, yield without loss of weight exactly the same product, viz. a glass of the same green colour and the same degree of transparency as the crystallized minerals—but softer, and having a sp. gr. of only 2·95; so that in passing from the crystalline to the amorphous state garnet suffers an expansion of about one-fifth, and vesuvian of about one-seventh. The glass is also easily soluble in hydrochloric acid, which is not the case with either of the minerals. [*Comp.* Magnus, (*Pogg.* 20, 477; 21, 50; 22, 391); Hess (*Pogg.* 45, 341); Varrentrapp (*Pogg.* 45, 343.)]

Axinite has a sp. gr. of 3·294, and is but very imperfectly decomposed by acids; after fusion, which takes place without loss of weight, it has a sp. gr. of 2·815, and is then easily dissolved by acids; this greater solubility it acquires even at a heat not sufficient to fuse it, but only to bake it together. (Rammelsberg, *Pogg.* 50, 363.)

Many other crystalline siliceous minerals not soluble in acids become so by fusion, probably from the same cause.

The following amorphous bodies, on the contrary, appear to be brought into the crystalline state when subjected to a heat not sufficient to melt them. In undergoing this change they exhibit, as first observed by Berzelius, a vivid *incandescence*, commencing at the point most strongly heated and extending through the entire mass; they are after-

wards found to possess greater specific gravity, greater hardness, and less solubility. The incandescence here observed is similar to the phenomena observed by Graham and Regnault (pp. 104 and 106). Most of the bodies which exhibit this phenomenon are originally crystalline, but when heated become porous and amorphous in consequence of losing water, ammonia, or other volatile matters: then, when no farther loss of weight takes place, if they are heated to a temperature a little below redness, they exhibit the incandescence just spoken of. To this class belong—the hydrates of zirconia, titanic acid, tantalic acid, molybdous oxide, oxide of chromium, peroxide of iron, and oxide of rhodium; also hydrated basic perarseniate of iron, hydrated antimonite of cobalt, hydrated antimoniate of cobalt, hydrated antimoniate of copper, and euxenite (which chiefly consists of hydrated tantalate of yttria.) If these compounds are heated merely to the point at which they part with all their water, they are afterwards nearly as soluble as in their hydrated state; but if by stronger heating incandescence has been produced, they are afterwards found to be much less soluble, and often alter in colour. Zirconia, after being heated to incandescence, is no longer soluble in any acid excepting boiling oil of vitriol; oxide of chromium after ignition is of a paler green than before, and soluble in nothing but boiling oil of vitriol; ignited peroxide of iron is as hard and as difficultly soluble as micaceous iron ore, which is crystallized peroxide of iron. The abovementioned antimonites and antimoniates are in their original state easily decomposed by hydrochloric acid, but after ignition they resist its action almost entirely, and are also of a much paler colour than before. Hydrated phosphate of magnesia and ammonia, after being deprived of all its water and ammonia by gentle heat, exhibits incandescence when more strongly heated. The same appearance is presented by the carburet of iron which remains in the distillatory apparatus after gently heating prussian blue or protocyanide of iron.

Gadolinite (silicate of yttria) whose conchoidal fracture and obsidian-like appearance testify sufficiently to its amorphous structure, (although some persons have fancied that they could discover a crystalline structure in it,) exhibits vivid incandescence when moderately heated; it sustains thereby no loss of weight, but is afterwards found to dissolve but very imperfectly in hydrochloric acid even after several days' boiling, although before ignition it is very easily soluble. According to Kobell (*J. pr. Chem.* 1, 91), its specific gravity increases by this change only from 4·25 to 4·31. Th. Scherer also (*Pogg.* 51, 493) observed in the gadolinite of Ytterby but a very trifling increase of specific gravity, but he attributes this circumstance to the partially distingrated and impure condition of the mineral; for (*a*) gadolinite from Hitterön, (*b*) orthite from Fille-Fjeld, and (*c*) allanite from Jotun-Fjeld (which two minerals have nearly the same composition as gadolinite) showed after ignition considerable increase of density; the sp. gr. of *a* increased from 4·35 to 4·63, giving a condensation of 1000 to 9395; that of *b* from 3·65 to 3·94, therefore condensation = 9264; and of *c* from 3·54 to 3·76, therefore condensation = 9417. The quantity of water lost by *a* was 0·18 per cent., that lost by *b* and *c* was greater. At the same time *a* lost by ignition its black colour and opacity, becoming bottle-green and translucent. Scherer endeavours to explain the increase of density by supposing that the spherical atoms are at first disposed one upon another in such a manner that each spherule rests upon two others below it, and that the atoms after being heated are so displaced that each one of them rests upon three below it; this would give a condensation of from 1000 to 9432.

Perhaps also the fact of gypsum dehydrated by gentle heat becoming hard when mixed with water, and the non-production of this effect if the gypsum has been strongly burnt, may be explained by supposing that this substance when deprived of its water by a moderate heat is in the amorphous, but after strong ignition in the crystalline state.

b. Differences in the properties of compounds, probably arising from the different grouping of the Simple Atoms *which make up a compound atom.*

In considering the different properties of compound bodies resulting from dimorphism and amorphism, the structure of the compound atoms has been supposed to continue unaltered, and the occurrence of this or that crystalline form, or of the amorphous state, to depend solely on the manner in which these compound atoms are arranged amongst themselves. Hence it follows that these dimorphous and amorphous conditions may occur in simple bodies also, since simple atoms as well as compound ones may be disposed amongst themselves in various ways,—moreover that these several conditions (with perhaps some exceptions requiring further investigation) may be destroyed by fusion, evaporation, or solution of the solid body in which they exist; and it will then depend upon circumstances in what particular state the body will resume its solid form.—But it is otherwise with the differences now to be considered, the cause of which we shall assume to be that the manner or number in which simple atoms combine to form a compound atom may differ in different substances. It is easy to see that the various conditions hereby produced can occur only in compound bodies, and may remain unaltered by the passage of a body from the solid to the fluid state or *vice versâ;* for the compound atoms once constructed in this or that particular way may, without disturbance of internal structure, form fluid compounds with heat or with ponderable solvents. With this difference of grouping of simple atoms in the formation of compound atoms are connected many striking differences not only in the physical properties but also in the chemical relations of the bodies concerned.

α. Isomerism.

When two or more compounds which exhibit different physical and chemical relations, are so constituted that their compound atoms must contain the same elements combined according to the same numbers of simple atoms, and there is no ground for supposing that their proximate elements are of different natures, these compounds are said to be isomeric (using the word in its narrowest sense). It is supposed that the simple atoms which form a compound atom are put together in different ways.

Many of the compounds formerly classed under this head are now regarded as polymeric; it is only with regard to phosphoric acid, tellurous acid and telluric acid, peroxide of tin, and tartaric acid, that isomeric conditions are at present recognized; and even these bodies may with more or less probability be regarded as polymeric.

Phosphoric acid, $P O^5$, exhibits the three isomeric states of ordinary, pyro—and meta-phosphoric acid. Among the many diversities exhibited by these three acids, the most remarkable is that they saturate different quantities of a salifiable base. $P O^5$ in the state of ordinary phosphoric acid saturates 3 atoms of a base, in the state of pyrophosphoric is situates 2 atoms, and in the state of metaphosphoric acid only 1 atom. If 1 atom of $P O^5$, in whichever of the three states it may

happen to be, is ignited with three atoms of any base, soda for instance, an ordinary phosphate is produced; but when P O^5 is ignited with 2 atoms of soda, the result is a pyrophosphate, and with 1 atom a metaphosphate. By long digestion or boiling with a large quantity of water, which itself acts as a base, the pyrophosphates and metaphosphates are converted into ordinary phosphates. The particular quantity of base with which P O^5 is in contact, seems then at certain high temperatures to affect the manner in which 1 atom of phosphorus arranges itself with respect to 5 atoms of oxygen, so that the compound is capable of saturating sometimes 3 atoms of a base, sometimes 2, and sometimes only one. If we would explain these remarkable relations of phosphoric acid first discovered by Graham on the hypothesis of Polymerism, we might consider ordinary phosphoric acid as P O^5, pyrophosphoric acid as P^2 O^{10}, and metaphosphoric acid as P^2 O^{15}; then P O^5 would saturate three, P^2 O^{10} four, and P^3 O^{15} three atoms of a base. (*Vid.* Phosphorus.)

In the case of tellurous acid, Te O^2, a more soluble modification A and a less soluble modification B are to be distinguished: the latter is produced by the action of nitric acid upon A, and is again converted into A by fusion with caustic potash. Telluric acid, Te O^3, exhibits two modifications perfectly similar to the above; the more soluble of the two is converted into the less soluble, when two or more atoms of it are fused with one atom of potash; this is analogous to the transformations of phosphoric acid above noticed. If these compounds are regarded as polymeric, they must be supposed to exist as Te O^2, Te^2 O^4, Te O^3 and Te^2 O^6. (*Vid.* Tellurium.)

Antimonious and antimonic acid may possibly pass from one such modification to the other when their salts are ignited.

Peroxide of tin, when precipitated by caustic alkalis from a solution of the bichloride, is much more easily soluble in acids than the anomalous variety of it produced by the action of nitric acid upon metallic tin; the latter when dissolved exhibits also very different relations. Possibly the soluble oxide may be Sn O^2 and the anomalous variety Sn^2 O^4.

Among organic compounds the following may be regarded as isomeric: Tartaric and racemic acid (C^2 H^2 O^3);—mucic and paramucic acid (C^6 H^4 O^7);—maleic and paramaleic acid (C^4 H O^3).

β. *Polymerism.*

Two or more compounds possessing different physical and chemical properties, and composed of the same elements in the same proportions are said to be polymeric, when their differences may be explained by supposing that their compound atoms contain different numbers of simple atoms, varying however in such a manner that the numerical ratio of the several kinds of simple atoms remains unaltered. If for example one of a group of polymeric compounds contains 1 atom of a substance A and 3 atoms of a substance B, then the second may contain 2 atoms of A and 6 atoms of B, the third 3 atoms of A and 9 atoms of B and so on. In such cases the weight of the compound atom varies, but the proportions between its elements remains the same.

Besides the instances mentioned under Isomerism, which ought all perhaps to be included under this head, the following among organic combinations must be particularly noticed.

Polymeric compounds all containing 1 part of hydrogen united with 6 parts of carbon, and therefore containing C H: Olefiant gas, the more volatile oil of oil-gas, rock-oil, eupion, oil distilled from bees'-wax, caout-

choucine, heveene, oil of wine, stearoptin of oil of roses, paraffin, cetine, &c. Olefiant gas is probably $C^4 H^4$, cetine $C^{32} H^{32}$.

Benzin, oilgas-camphor, and scheererite are $C^2 H$.

The oils of turpentine, juniper, copaiba, lemons, and black pepper are $C^5 H^4$.

Naphthaline and paranaphthaline are $C^3 H^2$.

Idrialine and Vogel's amber-camphor are $C^3 H$.

Methylic ether is $C^2 H^3 O$; alcohol $C^4 H^6 O^2$.

Cyanogen is $C^2 N$, paracyanogen probably $C^6 N^3$.

Cyanic acid is $C^2 N O$, fulminic acid probably $C^4 N^2 O^2$, cyanuric acid $C^6 N^3 O^3$.

Volatile chloride of cyanogen is $C^2 N Cl$, the fixed chloride probably $C^6 N^3 Cl^3$.

γ. *Metamerism.*

This term is applied by Berzelius to the case in which the compound atoms of two chemical compounds containing the same elementary atoms, and for the most part in the same proportions, are nevertheless made up of different proximate elements. According to this definition metameric bodies must always belong to the higher orders of compounds. In some cases one only of the bodies concerned is a compound of a higher order.

It is only among organic bodies that metameric compounds occur. The following are the most important:—

	C	H	O
Acetic acid	4	3	3
Water		1	1
Glacial acetic acid	4	4	4
Formic acid	2	1	3
Ether	4	5	1
Formic ether	6	6	4

	C	H	O
Formic acid	2	1	3
Methylic ether	2	3	1
Formiate of methylic ether	4	4	4
Acetic acid	4	3	3
Methylic ether	2	3	1
Acetate of methylic ether	6	6	4

Formic ether and acetate of methylic ether have the same specific gravity when in the form of vapour, and nearly the same specific gravity and boiling point when in the liquid state: but in other respects they are totally different; the former, when treated with caustic potash, is resolved into formiate of potash and alcohol, the latter into acetate of potash and wood-spirit.

The differences between the several compounds produced by the action of sulphuric acid upon alcohol, viz. sulphovinic acid, ethionic acid, isethionic acid, &c. are probably dependent on metameric conditions.

[For some examples adduced by Laurent, *vid. Ann. Chim. Phys.*, 66, 175.]

Aldehyde is $C^4 H^4 O^2$, and its vapour weighs 1·5317; acetic ether, which is composed of acetic acid ($C^4 H^3 O^3$) and ether ($C^4 H^5 O^1$) is $C^8 H^8 O^4$; and both its atomic weight and the spec. grav. of its vapour are twice as great as those of aldehyde.

When cyanic acid is mixed in the cold with aqueous solution of ammonia, cyanate of ammonia is produced, as proved by the fact that the liquid yields cyanic acid when treated with sulphuric acid, and ammonia when treated with potash. But warming, or even spontaneous evaporation, is sufficient to convert the salt into urea, which does not exhibit these reactions with sulphuric acid and potash. Urea is $C^2 N^2 H^4 O^2$; the

same atoms would give 1 atom of cyanate of ammonia and 1 atom of water, viz., $N H^3$, $C^2 N O, H O$. Cyanate of ammonia is, therefore, converted into urea merely by a change in the arrangement of its atoms.

IV. Decomposition of Chemical Compounds.

Every chemical compound may, as far as we know, be resolved into its elements. Nevertheless it is possible that many substances hitherto undecomposed may be compounds of so intimate a nature that they have resisted all attempts which have as yet been made to decompose them. The resolution of a chemical compound into its elements is called *Decomposition;* the compound is said to be *decomposed;* it is resolved into heterogeneous substances, which might be called *Decomposition-substances.* (Zersetzungs-stoffe.) These are either *Educts* or *Products* of decomposition. They are called educts when they exist in the compound before decomposition, and form part of it; products, when they are generated during decomposition. Carbonic acid which is disengaged by the action of hydrochloric acid upon carbonate of lime, is an educt; but the same acid, when evolved by heating charcoal with red oxide of mercury, is a product. Products are always compound bodies; educts may be either simple or compound,—the latter, when the decomposing body (*e. g.*, carbonate of lime) contains proximate as well as ultimate elements. According to the mode of decomposition, sometimes only educts are obtained (water decomposed by the electric current), sometimes only products (water decomposed by phosphuret of calcium), sometimes both together (water decomposed by potassium).

1. *Conditions of Chemical Decomposition.*

In order that a compound may be decomposed, the forces which bind its elements together must be overcome by stronger forces. The greater number of decompositions are brought about by the action of stronger affinities; other natural forces may, however, concur in producing the effect.

A. No chemical combination of ponderable bodies can be overcome by *pressure:* but compounds of ponderables with imponderables, as heat, may be decomposed by that kind of force. Water may be pressed out of a sponge, a proof that pressure can overcome combination produced by adhesion: but the strongest pressure fails to separate water from gypsum and other salts containing water of crystallization, provided the temperature does not rise to the melting point of the salt. It has, indeed, been affirmed that lead amalgam, and some other amalgams, give up a portion of their combined mercury when subjected to pressure; but the mercury thus pressed out is only that which is in excess, and remains in the liquid state adhering to the particles of the solid compound. On the other hand, vapour of water is resolved by pressure into liquid water and heat: perhaps also the development of heat, light, and electricity by pressing and rubbing various substances is an effect of a similar nature.

B. *Gravitation.*—When a light and a heavy substance are contained in a fluid compound, it might be supposed that after long standing the former would settle at the top and the latter towards the bottom, so that even if complete separation did not take place, the upper part of the fluid would be richer in the lighter material, and the lower in the heavier: no such effect however is actually observed.

It is said that in the vessels used to hold the concentrated liquid of the salt-works, the upper portions are found to be less rich in salt than

the lower. Since, however, these vessels are not always filled with one and the same liquid, but are charged from time to time with solutions of various degrees of strength, the less concentrated portions dispose themselves above the more concentrated, and the liquor being left at rest, uniform mixture does not take place for a long time. Similarly, brandy kept in casks is said to contain a greater proportion of spirit in the upper, and of water in the lower part. Here, again, the question may be raised whether the cask has not been filled with successive portions of brandy of different strengths, which have disposed themselves in layers one above the other. Leblanc (*J. Phys.*, 33, 376) found that if in a saturated solution of any salt crystals of the same salt are placed, some in the upper part of the liquid and others at the bottom, the former gradually dissolve while the latter increase in the same ratio, and ultimately the crystals at the bottom of the liquid decrease at their upper and increase at their lower part. This effect is attributed by Berthollet (*Stat. Chim.* 1, 49,) to a sinking of the particles of the salt by their own weight; it may, however, without difficulty, be explained by observing that the upper strata of air surrounding the vessel are warmer than the lower, and, consequently, that the upper portions of the liquid become warmer than the lower, and dissolve the salt immersed in them: hence these portions of the liquid become heavier, and sink to the bottom, where they become cooler, and deposit part of their salt in crystals. Lastly, it is very difficult to obtain flint-glass of perfectly uniform constitution; the lower part is generally much richer than the upper in oxide of lead. But this, again, does not prove the sinking of the heavier material out of a perfectly homogeneous mixture. For when a mixture of oxide of lead, alkali, and silica is heated, the oxide of lead melts first, and sinks before it has entered into uniform combination with the other ingredients. These latter subsequently melt: but since liquids of different specific gravities mix but slowly when at rest, and in this case, moreover, the great viscosity of the melted mass presents a further obstacle to the mixture, uniformity can only be produced by repeated and careful stirring. But when this end has once been attained, it is probable that the glass will continue uniform, even when kept for a long time in a state of fusion. That such is the case appears from Faraday's directions for the preparation of flint-glass; as also from the statement of Frauenhofer, that he obtained a mass of flint-glass weighing 400 lbs., of perfectly uniform constitution throughout. Now, when we consider the long time which such a mass would occupy in cooling, such a result could scarcely be credited if it were admitted that oxide of lead could sink to the bottom of a mass once obtained in a state of uniformity.

C. *Cohesion* appears to exert a much more decided influence on the decomposition of chemical compounds, at least of the less intimate kind.

The hitherto received theory on this matter is as follows. When a solid body dissolves in a liquid, the cohesion of the solid acts in opposition to the dissolving power of the fluid; the two forces tend to equilibrate each other; and in proportion as the fluid takes up more and more of the solid, its tendency to dissolve a further quantity—or, in other words, its affinity for the solid—diminishes and ultimately becomes no greater than the cohesion of the solid or the tendency of its particles to remain united amongst themselves,—and then the process of solution stops. But the cohesion of a solid body is generally diminished by elevation of temperature; consequently, when the fluid is heated up to a certain point, a further solution usually takes place, till by the new addition of the solid

body the affinity of the fluid for it is so far diminished that equilibrium between that force and the cohesion of the solid is again established. If now a solution thus saturated while warm be cooled down to its former temperature, the solid body regains its original cohesive power, and a portion of it separates from the fluid in order to unite in larger and usually crystalline masses, the quantity remaining in solution being only just so much as the fluid would directly have taken up at this lower temperature. This separation is called *Spontaneous* or *False Precipitation*, *Præcipitatio spontanea*, in so far as it takes place without the addition of a foreign body to the solution.

This precipitation by cooling is exhibited by the solutions of most salts in water and alcohol, of many kinds of camphor and fat in alcohol and ether, &c. Aqueous solutions containing excess of water often when cooled below 0° C. deposit a portion of the water in the form of ice, the remaining liquid being a concentrated solution of the salt; for at low temperatures the cohesion of ice may overcome its affinity for the salt. Whereas therefore a saturated solution when cooled deposits salt, so on the other hand a dilute solution, when its temperature is sufficiently reduced, yields ice. Lastly, a saturated solution of common salt solidifies at — 20° C. to a mixture of ice and common salt containing water of crystallization.—Glacial acetic acid solidifies at + 15° C. (59° Fah.); a mixture of this substance with $\frac{1}{9}$ water deposits glacial acetic acid at a lower temperature, the remaining liquid being a compound of glacial acetic acid with water; when the quantity of water is somewhat greater nothing solidifies; when it is still greater, part of it freezes leaving a more concentrated acid behind. When the mixture of glacial acetic acid with $\frac{1}{9}$ water, instead of being cooled, is subjected at 15° C. to a pressure of 1100 atmospheres, $\frac{1}{3}$ of it crystallizes in a few minutes in the form of glacial acetic acid. (Perkins, *Schw.* 39, 161.) It appears from this that increased pressure has the same effect as cold in increasing cohesion.

The following are exceptions to the law just considered. Some solid bodies, as lime and citrate of lime, are more soluble in cold water than in hot; so that a solution of either of them saturated in the cold becomes turbid when warmed, and clear again on cooling. If to a solution of chloride of calcium or nitrate of lime in absolute alcohol, there be added as much ether as will throw down only a portion of either of these salts, the mixture of alcohol and ether will become turbid, even to opacity—from precipitation of the limesalt still remaining in solution—every time the liquid is warmed, if only by the hand, but will regain its transparency on cooling. (Döbereiner, *Ann. Pharm.* 14, 249.) A solution of caustic potash in water dissolves in the cold a large quantity of tartrate of lime; the clear solution coagulates to a pasty mass when heated, but becomes clear and fluid again on cooling. (Lassonne, Osann.)—The solubility of Glauber's salt in water increases rapidly with rise of temperature up to 33° (92° Fah.), but diminishes when the temperature is raised above this point; water saturated with Glauber's salt at 33°, yields hydrated crystals when cooled, and anhydrous crystals when further heated.

Similar anomalies occur in solutions of liquids in other liquids. Coniin, agitated with water at ordinary temperatures, takes up a small portion of it: the clear liquid becomes turbid, from separation of water, every time it is warmed even by the hand, and clear again on cooling. (Geiger.)—Animin dissolves in 20 parts of water: the solution becomes turbid when heated, from separation of animin, which is redissolved on cooling. (Unverdorben.)—When a solution of chloride of calcium in a

mixture of water and acetone is heated, the acetone separates forming a film on the surface.—(Liebig and Pelouze, *Ann. Pharm.* 19, 287.)

The following observations of Gay-Lussac (*Ann. Chim. Phys.* 70, 407, also, *J. Pr. Chem.* 18, 193) render it doubtful whether cohesion plays so important a part in spontaneous precipitations as has been hitherto supposed, and raise a suspicion that this kind of precipitation is affected by difference of temperature in a manner which has not yet been explained. Cetine, paraffin, and stearic acid melt below the boiling point of alcohol, so that the quantities of them dissolved in that liquid at temperatures at which they are solid, can be compared with the quantities dissolved at temperatures at which they are liquid. From what precedes we should expect that these bodies would be much more soluble in the melted state than below their melting points, because the cohesion of a solid body is much greater than that of a liquid. But, according to Gay-Lussac, the solubility of these substances increases regularly as their temperature rises, without any sudden augmentation at the melting point. Gay-Lussac therefore considers that their solubility is unaffected by cohesion, and determined solely by temperature. Bodies exhibit the same relations in dissolving as in evaporating; vapour of water at 0° has the same tension, whether it be raised from water or from ice.

D. Some experiments seem to show that the feebler chemical combinations may likewise be overcome by *Adhesion.*

When vinegar is filtered through pure quartz-sand, the first portion of liquid that runs through is robbed of almost all its acid, and the vinegar does not pass through unchanged till the sand has become well charged with acid. Potato-brandy diluted with water and filtered through quartz-sand, yields at first pure water, then a mixture of water and alcohol deprived of its fusel-oil, and lastly the original mixture unaltered. Wood-shavings also at first deprive vinegar of nearly all its acid; charcoal acts still more powerfully. (Wagenmann, *Pogg.* 24, 600.) The last two substances may perhaps act by affinity.—Sömmering's experiment (*vid.* Alcohol), in which a mixture of water and alcohol enclosed in a bladder yielded on evaporation scarcely anything but water, may likewise be referred to the same class of phenomena, provided we suppose that the water is taken up by the bladder, not in consequence of affinity but of adhesion, and thus transferred to the outer surface, where it evaporates into the air.

E. A mode of decomposition not yet completely understood is that called *Action by Contact* (action de présence), or *Catalytic action.* These terms are applied by Berzelius and Mitscherlich to the case in which a solid or liquid body, when brought into contact with a compound, excites a decomposition of that compound (Catalysis)—without itself undergoing any alteration, mechanical or chemical,—or at all events, if a chemical alteration does take place,—without entering into combination with either of the elements of the compound. The Contact-substance or *Catalytic body* awakens by its mere presence, not by its affinity, the slumbering affinities of the elements, and causes them to assume a new arrangement involving more complete electro-chemical neutralization. Berzelius regards catalytic force as a peculiar manifestation of electro-chemical action.

The following instances may be referred to this mode of action. In peroxide of hydrogen, HO^2, the second atom of oxygen is retained by a very feeble affinity only, and escapes with effervescence even at ordinary temperatures. Many metals and oxides, when brought

in the state of powder in contact with this liquid, produce a violent disengagement of oxygen gas without themselves taking up oxygen or suffering any other alteration, excepting that some oxides, as that of silver, part with their own oxygen at the same time. This, according to Berzelius, is a case of catalytic action. The following explanation by Liebig is more probable (*Ann. Pharm.* 2, 22). Pulverulent and angular bodies accelerate the disengagement of a gas absorbed by a liquid (*vid.* Heat); they likewise exert this action on peroxide of hydrogen; this rapid escape of gas produces a rise of temperature, and this again accelerates the disengagement of gas,—and thus these actions continue to augment each other in intensity till the effervescence amounts to a slight explosion.—The following decompositions are also regarded as catalytic. The rapid decomposition of the aqueous solution of nitrosulphate of ammonia into nitrous oxide gas and sulphate of ammonia (which also takes place slowly by itself) by the action of spongy platinum, oxide of silver, &c.;—the separation of persulphuret of hydrogen, S^5H, into sulphuretted hydrogen, S H, which escapes as gas, and sulphur which remains behind, by contact with alkalis, chloride of calcium, &c.;—the resolution of alcohol into ether and water by the action of sulphuric acid;—that of sugar dissolved in water into carbonic acid and alcohol by ferments;—the conversion of alcohol into acetic acid by ferments;—the conversion of starch into sugar by dilute sulphuric acid or by diastase;—the conversion of urea dissolved in water into carbonate of ammonia by the action of animal mucus;—(*See these substances.*)—But the mode of action in these transformations sometimes admits of other explanations; and when this is not the case, our conception of it is by no means sufficiently clear to justify the positive assumption of this so-called contact-action or catalytic force, which, after all, merely states the fact without explaining it.

F. Just as a body in the act of combination may induce another to enter into combination at the same time (page 38), so likewise a compound in the act of decomposition may impart this decomposing activity to another. How and wherefore? we are unable to explain.

When peroxide of hydrogen by contact with oxide of silver gives up its second atom of oxygen, it likewise induces the oxide of silver to part with its oxygen. Vinous fermentation may be explained consistently with this view by supposing that the decomposing ferment brings the sugar into a state of decomposition, and the sugar is then resolved into carbonic acid and alcohol. A similar explanation may be applied to the decomposition of urea into carbonic acid and ammonia by animal mucus, of asparagin into aspartate of ammonia by yeast, and of amygdalin into hydrocyanic acid and other products of decomposition by the action of yeast and sugar (Liebig).

G. The *vital force* of plants and animals likewise exerts a decomposing action on chemical compounds.

The most remarkable instance of this is the action of light on the green parts of plants, causing them to decompose carbonic acid into oxygen and carbon, the latter of which elements combines with the hydrogen and oxygen of the vegetable juice producing numerous organic compounds.

H. But the most numerous and important decompositions of chemical compounds are those which are brought about by the action of other bodies, whose *superior affinity* produces new compounds at the same time that it destroys the old ones. For the production of these decompositions the same conditions are required as for the formation of chemical compounds (page 36); viz. immediate contact and the fluid state, at least of one of the bodies concerned,—whence fusion or vaporization by elevated

temperature is often a necessary preliminary;—and a distinction must be made between *decomposition in the wet way* and *decomposition in the dry way*.

Here also in some cases the fluid state is not essential. Thus lime decomposes sal-ammoniac when the two bodies are rubbed together in the dry state at ordinary temperatures; and common salt decomposes sulphate of mercury at a temperature below fusion. Borax also is decomposed when rubbed up with nitrate of lead, nitrate of silver, sulphate of zinc or sulphate of copper; so likewise is crystallized chloride of barium when rubbed up with nitrate of soda, a wet mass being formed by the separation of the water of crystallization of the borax or the chloride of barium. Again two solid substances insoluble in water may decompose one another when that liquid is present, provided the product which results from the decomposition is soluble in water; *e.g.* prussian blue and chalk or oxide of mercury.

On the other hand we often meet with this anomaly—that even when one of the bodies concerned is in the fluid state, decomposition does not take place till a certain quantity of water has been added. This phenomenon may in many cases be explained, according to Braconnot's view, by supposing that on the surface of the solid body there is formed a product of decomposition insoluble in a concentrated acid or its mixture with alcohol,—this product therefore forms a film which, though very thin, is impervious to the liquid and prevents further contact between the acid and the solid body; but when this film is dissolved by the addition of water the decomposition proceeds further. Whether in some of these cases, as supposed by Wetzlar, Schönbein, and others, electrical modifications of metals intervene by which they lose for a time their disposition to combine with oxygen,—is not yet satisfactorily determined.

Oil of vitriol mixed with a six-fold quantity of absolute alcohol will not decompose any dry carbonate. Absolute alcohol which has absorbed hydrochloric acid gas does not decompose carbonate of potash, but acts readily on other carbonates. Whilst dilute nitric acid gives up its oxygen to most metals with the greatest violence, the highly concentrated acid acts but very slightly upon bismuth and has no action whatever upon tin, iron, lead, or silver, these metals retaining their full metallic lustre when immersed in it. Iron is brought by strong nitric acid into a *passive* state so that it exerts no decomposing action even upon dilute nitric acid: it may however be brought back to its ordinary *active* state by various means, the impervious stratum on its surface being thereby removed, or a peculiar electric condition destroyed. Iron may be brought into the same state by immersion in a solution of nitrate of silver. Concentrated nitric acid does not decompose carbonate of lead, nor does it act on carbonate of lime or baryta even when boiling, most probably because the nitrates of lead, baryta and lime are insoluble in nitric acid; carbonate of potash on the contrary is rapidly decomposed by it, because nitrate of potash is easily soluble in strong nitric acid. But nitric acid mixed with absolute alcohol has no action on carbonate of potash, probably because nitrate of potash is insoluble in the alcoholic mixture; the carbonates of soda, baryta, and magnesia are slowly decomposed by it, those of lime and strontia immediately, possibly because the nitrates of lime and strontia are soluble in alcohol. Oxalic acid dissolved in absolute alcohol does not decompose carbonate of potash or of lime, but acts upon the carbonates of baryta, strontia, and magnesia (although the compounds of these last three bases with oxalic acid are insoluble [illegible] alcoholic mixture).

The alcoholic solution of racemic or tartaric acid does not decompose any salt of carbonic acid; that of citric acid does not decompose the carbonates of baryta, strontia, and lime; carbonate of magnesia is slowly decomposed by it, carbonate of potash more quickly. Glacial acetic acid does not decompose carbonate of lime even on boiling; it acts however on most other carbonates, but less quickly than when water is added. Glacial acetic acid mixed with absolute alcohol has no action on any carbonate till water is added to it. If both substances are liquid, no addition of water is necessary; thus oxalic acid in a state of efflorescence dissolved in absolute alcohol precipitates nitrate of lime dissolved in the same liquid. Further developments of this subject will be found under the heads of the above-named acids and metals, also under Alcohol. On the action of acids on metals, *vid.* Keir (*Schw.* 53, 154).—Herschel (*Ann. Ch. Phys.* 54, 87; *Pogg.* 32, 211, also *Ann. Pharm.* 10, 250).—Wetzlar (*Schw.* 49, 470; 50, 88 and 129; 56, 206).—Berzelius (*Annual Report*, 8, 104).—Schweigger Seidel (*Schw.* 53, 167).—Dumas (*Ann. de l'Industrie Fran.* 1829, Mai; abstr. *Schw.* 57, 23).—Schönbein (*Phil. Mag. J.* 9, 53; *Pogg.* 37, 390 and 590; 38, 444 and 492; 39, 137, 342 and 351; 40, 193; 41, 41; 43, 1).—Faraday (*Phil. Mag. J.* 9, 57; 10, 175).—Mousson (*Bibl. univ. N.S.* 5, 155; also *Pogg.* 39, 330).—Andrews (*Phil. Mag. J.* 12, 305; also *Pogg.* 45, 121).—Noad (*Phil. Mag. J.* 10, 267; 12, 48; 15, 292; abstr. *Pogg.* 15, 292).—On the action of acids on carbonates, *vid.* Berthollet (*Statique Chim.* 2, 50).—Pelouze (*Ann. Chim. Phys.* 50, 314, also *Pogg.* 25, 343, also *Ann. Pharm.* 5, 260;—*Ann. Chim. Phys.* 50, 434;—*J. Chim. med.* 9, 491).—Leroy (*J. Chim. med.* 9, 489).—Braconnot (*Ann. Chim. Phys.* 52, 286, also *Pogg.* 29, 173).—Kuhlmann (*Ann. Chim. Phys.* 67, 209, also *Ann. Pharm.* 27, 22, also *J. pr. Chem.* 14, 502).

Moreover, just as the simple formation of compounds often requires a higher temperature than that which is necessary to bring the combining substances into the fluid state, so likewise is this higher temperature necessary in many cases of combination attended with decomposition.—A red heat is necessary to enable oxygen gas to decompose ammoniacal gas into water and nitrogen gas, and for the formation of carbonic oxide and hydrogen gas by the action of charcoal on vapour of water.

In these cases also light and electricity may sometimes supply the place of elevated temperature (Vid. *Chemical effects of Light and Electricity*).

We proceed to notice some of the more important cases of chemical decomposition brought about by the superior affinity of superadded bodies:

1. A compound A B is decomposed by intervention of C into the compound A C and the liberated body B. (*Scheme* 1*.) *Simple Elective Affinity, Attractio electiva simplex.*

Decompositions of this kind in which heat forms one of the acting bodies are as follows: Let A B be water, *i.e.* heat + ice, and C frozen mercury; these give liquid mercury and ice (*Sch.* 2).—Let A B be oxide of gold, *i.e.* oxygen + gold, and C heat at a temperature of incandescence; the result is oxygen gas (oxygen + heat) and metallic gold (*Sch.* 3). In a similar manner carbonate of lime at a red heat is resolved into carbonic acid gas and lime: likewise arseniuretted hydrogen gas at a red heat into hydrogen gas—which in the separate state is more expanded and therefore probably combined with a greater quantity of heat than when in union

* Plate III. The dotted lines denote the compounds destroyed; the full lines the new compounds formed.

with arsenic—and metallic arsenic.—Let A B be hydrochloric acid gas (hydrochloric acid + heat), and C water; the water combines with the acid forming aqueous solution of hydrochloric acid, and heat is disengaged. (*Sch.* 4).

Cases in which all three bodies are ponderable: Sulphuret of silver exposed to the air at a red heat yields sulphurous acid and metallic silver (*Sch.* 5).—Oxide of zinc heated to redness in contact with charcoal is resolved into carbonic oxide and metallic zinc (*Sch.* 6).—Oxide of copper in a similar manner into carbonic acid gas and copper (*Sch.* 7).—Chlorine gas expels oxygen gas from red-hot potash (K O) and produces chloride of potassium (*Sch.* 8).—Hydrochloric acid and zinc form chloride of zinc with disengagement of hydrogen gas (*Sch.* 9).—Iron decomposes chloride of silver in contact with water into chloride of iron and silver (*Sch.* 10). Cinnabar (Hg S) heated to redness in contact with iron yields sulphuret of iron and mercury (*Sch.* 11).—Carbonic acid gas is expelled by sulphuric acid from carbonate of lime, and sulphate of lime is formed (*Sch.* 12).—Aqueous solution of nitrate of silver mixed with caustic potash yields oxide of silver and nitrate of potash (*Sch.* 13).—Water added to a solution of resin in alcohol forms dilute alcohol and precipitates resin. On the other hand, Glauber's salt dissolved in water is almost wholly precipitated by addition of alcohol: for the mixture of alcohol with a large quantity of water has scarcely any affinity for resin, and that of water with a large quantity of alcohol scarcely any affinity for Glauber's salt.

Sometimes C takes from the compound A B only a part of A, so that a compound of B with a smaller quantity of A is separated. Thus zinc in a state of incandescence robs carbonic acid of half its oxygen and converts it into carbonic oxide (*Sch.* 14).—The resulting compound A C may then combine with A B which has been deprived of half its original quantity of A. Thus zinc and solution of sulphurous acid form hyposulphite of zinc (*Sch.* 15).—Or C may rob the compound A B of the whole of A and part of B, and separate only the remaining part of B. Thus sulphuric acid heated with peroxide of manganese forms sulphate of protoxide of manganese and drives out half the oxygen (*Sch.* 16).

The decomposition of A B by C sometimes takes place in presence of another body D which is at first combined with A B and afterwards unites with A C. Water (A B) mixed with sulphuric acid (D), yields when acted upon by zinc, sulphate of zinc and hydrogen gas (*Sch* 17).—The same kind of action takes place whenever hydrogen gas is given off during the solution of a metal in dilute oxygen acids or alkaline solutions.—To this head likewise belong all precipitations of metals from solutions of their oxides in ox-acids or alkalis, by other metals in the metallic state: (in *Sch.* 17 a metal must be substituted for hydrogen). Thus zinc immersed in sulphate of copper produces sulphate of zinc and metallic copper (*Sch.* 18): similarly, copper and nitrate of silver give nitrate of copper and metallic silver (*Sch.* 19).—When carbonate of soda is heated to redness in contact with phosphorus, phosphate of soda and charcoal are produced (*Sch.* 20).

Sometimes only part of the compound A B is decomposed, and the other part combines with the newly-formed compound A C, taking the place of the substance D. Potassium heated in carbonic acid gas separates charcoal and forms potash, which combines with the undecomposed portion of the carbonic acid (*Sch.* 21).—Chlorine passed into solution of ammonia liberates the nitrogen of that c[illegible]n the gaseous form,

and combines with the hydrogen forming hydrochloric acid, which then unites with the remaining portion of ammonia, forming sal-ammoniac (*Sch.* 22).

A similar action sometimes takes place, with this difference, that C takes only part of A from the decomposing portion of A B. Mercury heated with sulphuric acid produces sulphate of mercury and sulphurous acid (*Sch.* 23).—Copper treated with nitric acid yields nitrate of copper and nitric oxide gas (*Sch.* 24).—Zinc and dilute nitric acid yield nitrate of zinc and nitrous oxide gas (*Sch.* 25).

2. The action of C on the compound A B produces two new compounds, A C and B C (*Sch.* 26). When oxide of mercury is heated to redness, vapour of mercury (mercury + heat) and oxygen-gas (oxygen + heat) are produced. Sulphuret of carbon burnt in oxygen gas produces sulphurous acid and carbonic acid (*Sch.* 27).—Sulphuret of antimony heated in contact with air yields sulphurous acid gas and antimonious acid (*Sch.* 28).—A similar action takes place with other metallic sulphurets.—Chlorine gas converts sulphuret of antimony into chloride of sulphur and chloride of antimony (*Sch.* 29), and produces similar effects on other metallic sulphurets.—Sometimes the two new compounds A C and B C combine together. Thus sulphuret of copper when heated in the air is converted into sulphate of oxide of copper (*Sch.* 30).

The same decomposition often takes place in presence of a fourth body D combined with A B, one of the new compounds A B and A C, or each of them separately, uniting with this fourth body.—Mercury placed in a solution of nitrate of silver forms subnitrate of mercury and silver-amalgam (Arbor Dianæ, *Sch.* 31).—When phosphorus is boiled in water holding potash in solution, phosphate of potash and phosphuretted hydrogen gas are produced (*Sch.* 32).—Chlorine gas passed into aqueous solution of potash yields chlorate and hydrochlorate of potash (*Sch.* 33).—If in this process we suppose that potash instead of water is the body decomposed, and that not hydrochlorate of potash but chloride of potassium is produced, then *Sch.* 34 must be substituted for *Sch.* 33. The action of bromine or iodine upon potash is precisely similar to that of chlorine. Sulphur exerts a similar action on lime (or potash) when water is present; the action will be represented by *Sch.* 35 or *Sch.* 36 according as we suppose hydrosulphate of lime or quinto-sulphuret of calcium to be the body formed. In *Sch.* 34 and 36, the fourth body is a part of the compound A B, which remains undecomposed. The same is the case in the conversion of potash by excess of sulphur at a red-heat into quinto-sulphuret of potassium and sulphate of potash (*Sch.* 37).

Sometimes a fourth body D exists before the decomposition in combination with A B, and is set at liberty by the decomposition. Sulphate of ammonia dissolved in water is converted by chlorine into hydrochloric acid, chloride of nitrogen, and free sulphuric acid (D) (*Sch.* 38).

3. The compound A B is acted upon by the compound C D, and there are formed two new compounds A C and B D. This very frequent and important case is called decomposition by *Double Elective Affinity*, *Double Affinity*, *Attractio electiva duplex* (*Sch.* 39).

Perchloride of phosphorus (PCl^5) and water produce hydrochloric acid and phosphoric acid (PO^5) (*Sch.* 40).—Sulphuretted hydrogen with oxide of lead yields sulphuret of lead and water (*Sch.* 41); with peroxide of tin, bisulphuret of tin and water (*Sch.* 42); with arsenious acid, ter-sulphuret of arsenic and water (*Sch.* 43); with arsenic acid, quinto-sulphuret of arsenic and water (*Sch.* 44).—Other hydracids act upon me-

tallic oxides in a similar manner. Tersulphuret of antimony heated with protochloride of mercury yields terchloride of antimony and proto-sulphuret of mercury (*Sch.* 45).

The most frequently occurring decompositions by double affinity are those of salts (containing a base and an acid as proximate elements). Two salts which contain different acids and different bases often interchange elements in such a manner that the acid of the first combines with the base of the second, and the acid of the second with the base of the first. This decomposition is seldom observed when salts are melted together, because in case of an exchange taking place the two newly formed salts often fuse together; but it very frequently occurs when solutions of the salts in water or other liquids are mixed together. In the latter case if the two newly-formed salts are likewise soluble, the decomposition may be discovered from the constitution of the crystals obtained on evaporation or cooling; but in very many cases one of the newly-formed salts is but slightly or not at all soluble in the menstruum, and consequently affords evidence of the decomposition by separating from the solution in the solid form. When aqueous solutions of carbonate of potash and sulphate of soda are mixed, the liquid yields on evaporation and cooling, first crystals of sulphate of potash, afterwards of carbonate of soda (*Sch.* 46).—Nitrate of baryta and sulphate of soda mixed in the state of aqueous solution yield nitrate of soda which remains dissolved, and sulphate of baryta which immediately precipitates in the form of an insoluble white powder (*Sch.* 47).—Similarly, aqueous solutions of carbonate of potash and nitrate of lime yield a thick precipitate of carbonate of lime, while nitrate of potash remains dissolved in the liquid (*Sch.* 48).—A soluble salt may likewise interchange elements with an insoluble one; *e. g.* carbonate of soda and sulphate of lead yield sulphate of soda and carbonate of lead.

To this case belongs Richter's *Law of Neutralization* (Beiträge, 4, 66). Richter found that when decomposition takes place between two salts which are neutral to vegetable colours (page 97) the two newly-formed salts are likewise neutral. From this he concluded that if the acid of the first salt, by combining with a certain quantity of the base of the second, sets free a certain quantity of acid belonging to it, this quantity of acid is exactly sufficient to form a neutral salt by combining with the disposable quantity of the base of the first. Of this important principle Richter availed himself in his stoichiometrical calculations: the result can now be easily explained by the atomic theory as above developed. Salts are commonly neutral when they contain one atom of acid for every atom of base. If now two salts thus constituted decompose each other, precisely 1 atom of acid of the first combines with 1 atom of base of the second; and 1 atom of base of the first with 1 atom of acid of the second: hence both the new compounds are neutral. In those cases, however, in which the newly formed insoluble salt contains a number of atoms of a particular acid different from that which occurs in the former salt, the law of neutralization is subject to exceptions. Thus ordinary phosphate of soda contains 1 atom of phosphoric acid and 2 atoms of soda: now when this is decomposed by nitrate of silver (1 atom of acid + 1 atom of base) a compound is precipitated containing 1 atom of phosphoric acid and 3 atoms of oxide of silver; but these were originally combined with 3 atoms of nitric acid, and they now come in contact with only 2 atoms of soda, and since 2 atoms of soda require only 2 atoms of nitric acid to neutralize them, the liquid becomes acid (*Sch.* 49).

The following are cases of decomposition by double affinity, in which

a fifth body E also comes into play. The compound A B is in combination with E and the latter subsequently unites with A C. Oil of vitriol (sulphuric acid + water) mixed with chloride of sodium yields sulphate of soda and hydrochloric acid gas (*Sch.* 50).—Sulphate of mercury heated with chloride of sodium yields sulphate of soda and chloride of mercury (*Sch.* 51).—By fusing together sulphate of baryta and chloride of calcium we obtain sulphate of lime and chloride of barium (*Sch.* 52).—In a similar manner may be explained all other decompositions of a salt consisting of an oxacid and a base by any metallic sulphuret, iodide, bromide, chloride, fluoride, or cyanide, whether water be present or not. Thus aqueous solutions of sulphate of soda and chloride of barium yield, on mixing, a precipitate of sulphate of baryta, while chloride of sodium remains in solution (*Sch.* 53); and solutions of carbonate of potash and chloride of calcium yield precipitated carbonate of lime and soluble chloride of potassium (*Sch.* 54). If however we suppose that the metallic sulphurets, chlorides, &c., are converted on solution into salts consisting of hydracids combined with metallic oxides, then *Sch.* 54 must be altered into *Sch.* 55.—The mutual decomposition of ferrocyanide of potassium and sulphate of copper may be represented by *Sch.* 56 or *Sch.* 57, accordingly as it is supposed that the former dissolves in water without alteration, or becomes changed into prussiate of protoxide of tin and potash; in the former case both A B and C D are combined, the one with a fifth, the other with a sixth body, the former of which combines with A C, the latter with B D.

The decomposition of common salt by heating it with silica, and allowing vapour of water to have access to the mixture, presents this peculiarity—that E the silica is not combined with A B the water, but acts by itself and combines with A C the soda (*Sch.* 58).

In some cases of decomposition by double affinity, part of the compound A B remains undecomposed and enters into combination with the new compound A C. When 2 atoms of baryta at a red heat are acted upon by 1 atom of bisulphuret of carbon, there are formed 2 atoms of sulphuret of barium and 1 atom of carbonic acid which unites with the undecomposed atom of baryta (*Sch.* 59).—In other cases the undecomposed portion of A B unites partly with A C and partly with B D. Thus when tersulphuret of antimony in excess is fused with potash, a compound of sulphuret of antimony with oxide of antimony is formed, and also a compound of sulphuret of antimony with sulphuret of potassium (*Sch.* 60).

Or again, the undecomposed portion of A B unites with the new compound B D, and the undecomposed portion of C D with the new compound A C. Thus on fusing together 8 atoms of tersulphuret of antimony and 7 atoms of potash, we obtain a compound of sulphuret of potassium with sulphuret of antimony and a compound of oxide of antimony with potash (*Sch.* 61).—Bisulphuret of carbon dissolved in aqueous solution of potash yields sulphuret of potassium which unites with sulphuret of carbon, and carbonic acid which combines with potash (*Sch.* 62).

The compound A B may also be in combination with a fifth body E, which is set free by itself simultaneously with the formation of A C and B D. The compound of hydrochloric and ammonia (E) is resolved when mixed with lime into chloride of calcium and water, while ammonia is set free (*Sch.* 63.)

Lastly, a portion of B may remain uncombined: 2 atoms of hydrochloric acid and 1 atom of peroxide of manganese yield 2 atoms of water

and 1 atom of chloride of manganese, while 1 atom of chlorine is disengaged (*Sch.* 64). If we suppose that hydrochlorate of protoxide of manganese is formed instead of the chloride of manganese, we must represent the action by *Sch.* 73.

4. The mutual action of AB and CD produces only the compound A C, while both B and D are separated in the free state (*Sch.* 65). Carbonate of potash mixed in solution with sulphate of alumina forms sulphate of potash, while carbonic acid is disengaged as gas, and alumina precipitated, this earth not being able to combine with carbonic acid (*Sch.* 66). Nitric acid and hydrochloric acid heated together form water, hyponitric acid, and chlorine (*Sch.* 67). In this case the compounds A B and C D may exist in combination one with the other, and suffer decomposition when heated. Thus sulphate of ammonia passed through a red-hot tube is resolved into water, nitrogen gas and sulphur (*Sch.* 68). Moreover the element B of the compound A B and the element D of the compound C D may be identical: thus sulphurous acid and sulphuretted hydrogen form water and sulphur (*Sch.* 69); iodic acid and hydriodic acid yield water and iodine (*Sch.* 70); nitrite of ammonia dissolved in water is resolved by gentle warming into water and nitrogen gas (*Sch.* 71). If in these cases the body C does not take up the whole of A, part of the latter remains in combination with the separated element which existed in both the original compounds: thus nitrate of ammonia is resolved by heat into water and protoxide of nitrogen. (*Sch.* 72.)

A portion of A B may also remain undecomposed and combine as a fifth body with either D or A C. Hydrochloric acid and peroxide of manganese resolve themselves by their joint action into water, chlorine, and hydrochlorate of protoxide of manganese (*Sch.* 73). Anhydrous sulphuric acid acting with the aid of heat on chlorine of sodium produces sulphate of soda, sulphurous acid gas, and chlorine gas (*Sch.* 74).

5. The two bodies C and D act separately on the compound A B, and produce the compounds A C and B D. The two electricities flowing into water on opposite sides produce oxygen gas, which may perhaps be regarded as a compound of positive electricity with oxygen, and hydrogen gas, which should perhaps be regarded as a compound of negative electricity wite hydrogen (*Sch.* 75); and a similar explanation may be given of the decompositions of other ponderable compounds by the electric current. Silica mixed with charcoal and acted upon at a red heat by chlorine gas, yields chloride of silicium and carbonic oxide (*Sch.* 76). Similar results are obtained with many other metallic oxides.

6. There are two compounds A B and C D independent of each other: a body E combines with A, brings B into combination with D, and sets C at liberty (*Sch.* 77). When vapour of water is passed over a mixture of chloride of silver and charcoal at a red heat, carbonic oxide, hydrochloric acid, and metallic silver are produced (*Sch.* 78). In the following instance another portion of E combines at the same time with B D. Chloride of sodium, peroxide of manganese, and sulphuric acid yield sulphate of soda, sulphate of protoxide of manganese, and chlorine (*Sch.* 79).

7. From a compound of A B with A D, E takes the whole of A and separates B and D either in the free state or combined together (*Sch.* 80). When hydrate of potash is brought into contact with iron at a white heat, oxide of iron, hydrogen gas, and potassium are produced (*Sch.* 81). Charcoal decomposes carbonate of soda, producing 3 At. carbonic oxide gas and 1 At. sodium (*Sch.* 82). Charcoal at a red heat decomposes

phosphate of lead, producing carbonic oxide, phosphorus, and lead (*Sch.* 83). Hydrogen gas conducted over red hot sulphate of potash produces water and sulphuret of potassium (*Sch.* 84). Tin treated with aqueous solution of nitric acid yields peroxide of tin and ammonia, the latter, however, combining with the undecomposed portion of the nitric acid (*Sch.* 85).

8. Two compounds, A B C and D E F, resolve themselves by their mutual action into the 3 compounds A D, B E, and C F (*Sch.* 88). This case has received the name of *Attractio electiva multiplex.* Hydrosulphate of ammonia and nitrate of lead produce sulphuret of lead, water, and nitrate of ammonia (*Sch.* 87).

The cause of all these decompositions of existing compounds by superadded bodies resulting in the formation of new compounds, is universally to be sought in the condition that the forces which tend towards the formation of the new compounds are stronger than those whose tendency is to maintain the old ones. In such changes affinity plays by far the most important part; but some influence is also exerted by cohesion.

The influence of cohesion may perhaps be understood in the following manner. The more coherent any element of a compound may be, the greater will be its inclination to leave that compound, and form itself, by virtue of cohesion, into larger masses, and the more quickly, therefore, will the old compound be decomposed by a weaker affinity. The same effect results from greater cohesion in the new compounds; for the formation of these compounds is then assisted, not only by the affinity of their elements, but also by the tendency of the compound atoms to unite themselves by virtue of their cohesion into larger masses. The greater therefore the cohesion of the separating bodies and of the compounds about to be formed, the more easily will the decomposition take place; on the contrary, the greater the cohesion of the old compounds and of the body which produces the decomposition, the greater will be the excess of affinities required to effect that decomposition. This influence of cohesion seems to be especially corroborated by the law discovered by Hahnemann (*Demachy Laborant im Grossen*, P. 2, 1784, *Vorrede*), and further developed by Berthollet, viz., that two salts dissolved in water decompose one another by double affinity, whenever one at least of the new salts is, at the given temperature, less soluble (and therefore more coherent) than either of the two original compounds. This law holds good without any exception whatever; in no instance are two soluble salts produced from the mutual action of a soluble and an insoluble salt; on the other hand two soluble salts often produce a less soluble and an insoluble salt. The only case which appears to present an exception is that observed by Th. Scherer (*Pogg.* 51, 470), and this requires further examination. It is from this cause that precipitations so often result from decompositions by double affinity. (*Comp. Sch.* 46, 47, 48, 49.) If now we suppose that a salt dissolves in water with greater facility, the more coherent it is (although the strength of its affinity for water must also be taken into consideration), it will follow that in these decompositions the precipitation results from the greater cohesion of one or both of the new salts. Perhaps in these mutual decompositions of salts, the affinities by which the old compounds are held together are in equilibrium with those which tend to produce the new ones, and consequently the greater cohesion of a new compound determines the result.

On the other hand, the experiments of Gay-Lussac (page 114) must be considered, according to which cohesion exerts no perceptible influence on solubility. Nevertheless, Gay-Lussac's explanation of the above law

(*Ann. Chim. Phys.* 70, 427) differs but little from that of Berthollet. The following explanation may also be proposed. The more intimate the combination between an acid and a base, and consequently the more completely the combining tendency of the two bodies is satisfied by the combination, the smaller will be the affinity exhibited by the new compound, under otherwise equal circumstances, towards other bodies; it will therefore have less affinity for water, that is to say, it will be less soluble: it must, however, be observed that the solubility will diminish in very different degrees according to the nature of the acid and the base. Hence in the decomposition of salts by double affinity, the resulting compounds are always those in whose formation the strongest affinities come into play; and precisely for this reason, these same compounds are those which have comparatively the least solubility.

Independently, however, of this influence of the cohesive force (which must not in any case be estimated too highly), decompositions are wholly determined by the relative strength of the affinities. Decomposition invariably takes place whenever the *Separating Affinities, Affinitates divellentes, i. e.*, the affinities which tend to the formation of new compounds, are together greater than the *Latent Affinities, Affinitates quiescentes*, those, viz., by which the old compounds are held together. The result is determined not by any single affinity, but by the sum of all the affinities which are capable of being satisfied at the same time. Hence a stronger affinity may be overcome by several weaker affinities which can be brought to act together. For example, silica cannot be deprived of its oxygen by heating it with charcoal: whence it follows that the affinity of oxygen for silicium is greater than its affinity for carbon; neither can chloride of silicium be formed and oxygen separated by heating silica in chlorine gas; whence we may infer that silicium has a greater affinity for oxygen than for chlorine. But when chlorine gas is conducted over a mixture of silica and charcoal heated to redness, the affinities of oxygen for carbon and of chlorine for silicium act simultaneously, and these two weaker affinities are together greater than that of silicium for oxygen; consequently carbonic oxide and chloride of silicium are produced (*Sch.* 75).

From this may be deduced the explanation of *Decomposition by Predisposing Affinity* (*Affinitas prædisponens*). If the affinity between A and B be greater than that between A and C, it is still possible that C may decompose A B and form A C, provided a fourth substance D be present, whose affinity for A C is such as to determine the formation of that compound. Suppose the compound A B to be carbonic acid, C phosphorus, D soda. Phosphorus has not the power at any temperature of depriving carbonic acid of all its oxygen, and separating the carbon: on the contrary, when phosphoric acid and charcoal are heated together, carbonic oxide and phosphorus are produced. Now by the presence of soda, which has a certain affinity for carbonic acid, but a much greater affinity for phosphoric acid, the circumstances are altered. If vapour of phosphorus be conducted over carbonate of soda heated to redness in a tube, a black mixture of charcoal and phosphate of soda is produced, the action being accompanied by a development of light and heat (*Sch.* 20). If we suppose, for the sake of illustration, that the affinity of oxygen for carbon = 10, for phosphorus = 9, that of soda for carbonic acid = 1, and for phosphoric acid = 3, then the sum of the latent affinities will be 10 + 1 = 11, that of the decomposing affiniti[illegible] 3 = 12: consequently, decomposition must take place. In [illegible] it is the pre-

disposing affinity of soda for phosphoric acid which brings about the formation of that compound. It is true that we here take into account the affinity of a substance (soda) for a compound (phosphoric acid) which before the decomposition takes place has no existence. But when bodies are brought into intimate contact, all the forces which exist, not only in themselves but in all their possible compounds, are called into action at the same time. Without such a supposition it would be impossible to give a satisfactory explanation of the decomposition of carbonic acid by phosphorus, and of many others of similar nature.

The same decompositions always take place under similar circumstances; for example, it never happens that A B is decomposed by C at one time and A C by B at another; but with change of circumstances, such opposite results of the conflict of affinities often show themselves, constituting the so-called *Reciprocal or Alternating Elective Affinities, Affinitates reciprocæ.* The circumstances whose alteration may be attended with such changes of result are the relative quantities of the bodies which act upon each other, the predisposing affinity of the solvent, and the presence of heat.

1. *Relative Quantity.* An excess of one of the bodies which act upon each other may produce an opposite result, sometimes by adhesion, sometimes by affinity.

a. By Adhesion. When hydrogen gas is passed over black oxide of iron (Fe^3O^4), the oxide is reduced to the state of metallic iron, and a mixture of vapour of water and free hydrogen gas is discharged from the end of the tube. But if vapour of water be passed over this metallic iron, the metal is again converted into black oxide, and a mixture of hydrogen gas and undecomposed vapour of water issues from the tube. Gay-Lussac and Regnault (*Ann. Chim. Phys.* 1, 33; 62, 372) have shown that these opposite results are by no means produced (as some have supposed) by difference of temperature, but that at every degree of temperature from the dullest to the brightest red heat, and even when red-hot vapour of water is passed through the tube, the action takes place sometimes one way sometimes the other, according to the relative quantities of hydrogen gas and vapour of water present. Hydrogen has perhaps a greater affinity for oxygen than iron has; but at a red heat, the affinity of heat for hydrogen likewise comes into play, so that an equilibrium takes place, —and then the adhesion between hydrogen gas and vapour of water may determine the preponderance. If hydrogen gas is in excess, its adhesion to vapour of water causes formation of water and consequent reduction of iron: if vapour of water is in excess, its adhesion to hydrogen gas causes the iron to decompose part of the water, whereby it becomes oxidized and liberates hydrogen gas. In either case there is produced a mixture of hydrogen gas and vapour of water.—According to Despretz (*Ann. Chim. Phys.* 43, 222, also *Pogg.* 8, 159) zinc, tin, cobalt, and nickel act in the same manner as iron; and according to Regnault, uranium and cadmium do the same, although neither of them decomposes water with facility.—Zinc, tin, and iron exhibit, according to Regnault, precisely similar relations towards carbonic oxide and carbonic acid; they oxidate in carbonic acid gas and convert it into carbonic oxide; and on the other hand their oxides, when heated in a stream of carbonic oxide gas, are reduced to the metallic state, carbonic acid being at the same time produced. To explain this action, we must suppose adhesion to exist between carbonic oxide and carbonic acid gases.—Hydrogen gas passed in great excess over protosulphuret of tin produces tin and a mixture of hydrogen and sul-

phuretted hydrogen gases. (Elsner.) Tin heated in sulphuretted hydrogen gas produces protosulphuret of tin and hydrogen gas (Gay-Lussac & Thénard).—Hydrogen gas passed over red-hot chloride of silver produces silver and hydrochloric acid gas; on the other hand, when silver is heated to redness in hydrochloric acid gas, chloride of silver is produced and hydrogen gas set free (Boussingault, *Ann. Chim. Phys.* 54, 260). The disposing cause in this case must be the adhesion between hydrochloric acid gas and hydrogen gas.—If carbonate of lime be heated in a tube till it begins to give off carbonic acid gas, and the heat be then lowered to such a degree that the evolution of gas shall cease, it will immediately recommence on passing vapour of water or common air through the tube (Gay-Lussac, *Ann. Chim. Phys.* 63, 219, also *Ann. Pharm.* 22, 52). In this case, the adhesion between vapour of water or atmospheric air and carbonic acid gas enables the affinity of heat for carbonic acid to overcome, even at a reduced temperature, the affinity of lime for carbonic acid.—While carbonate of lime gives up its carbonic acid when heated to redness in the open air, quick lime on the other hand absorbs carbonic acid in great abundance when strongly ignited in an atmosphere of that gas (Petzholdt, *J. pr. Chem.* 17, 464).—Carbonic acid gas passed through an aqueous solution of bi-hydrosulphate of potash drives out all the sulphuretted hydrogen in the form of gas and forms bicarbonate of potash; on the contrary, sulphuretted hydrogen gas expels carbonic acid from bicarbonate of potash and forms bihydrosulphate of potash.—Metallic fluorides are decomposed by aqueous solution of hydrochloric acid, and metallic chlorides by aqueous solution of hydrofluoric acid. Hydrochloric acid decomposes the acetates and acetic acid the metallic chlorides. The decomposing acid must always be added in very great excess, so that a mixture of the decomposing and separated acids may be evolved in the state of gas or vapour (Gay-Lussac, *Ann. Chim. Phys.* 30, 291, also *N. Tr.* 12, 2, 260). In these cases, therefore, a certain influence is always exerted by the mutual adhesion of the elastic fluids, or according to Dalton's theory (page 22) by the circumstance of each of the elastic fluids acting as a vacuum towards the other.

b. By Affinity. If to an aqueous solution of 2 atoms of sulphate of ammonia, potash, or soda there be added 1 atom of nitric acid (a larger quantity would remain uncombined) the smell of the acid is completely destroyed, and when the solution is left to evaporate spontaneously, nitrate of ammonia, potash, or soda crystallizes out, and the mother-liquid contains an alkaline bisulphate. If on the contrary to an aqueous solution of 1 atom of nitrate of ammonia, potash, or soda there be added 2 atoms of sulphuric acid and heat applied to the mixture, the whole of the nitric acid escapes and an alkaline bisulphate remains. One atom of sulphuric acid would take up only half the alkali and drive out only half the nitric acid, unless the action were assisted by an elevated temperature. Hence nitric acid takes from neutral sulphate of ammonia, potash, or soda, the half of its base and forms a nitrate; the nitrate on the other hand is decomposed by excess of sulphuric acid. This may be explained as follows. The above-named alkalis can combine either with 1 atom of sulphuric acid to form neutral sulphates, or with 2 atoms to form bisulphates: with nitric acid they only combine according to equal numbers of atoms. Suppose the affinity of the alkali to nitric acid = 5, to the first atom of sulphuric acid = 6, and that of the neutral alkaline sulphate so formed to the second atom of sulphuric acid = 2 [illegible] nitric acid be added to a neutral alkaline sulphate, either one [illegible] sulphate will

remain undecomposed, affinity = 6; or its alkali will combine with the nitric acid, affinity = 5, and its sulphuric acid with the other atom of neutral sulphate, affinity = 2; the sum of these affinities is 5 + 2 = 7, and since 6 < 7, decomposition takes place (*Sch.* 88). The alkaline bisulphate thus formed is likewise undecomposable by any excess of nitric acid, because it is held together by the affinities 6 + 2 = 8, and the nitric acid acts upon it only with an affinity = 5. If therefore on the other hand two atoms of sulphuric acid act upon one atom of an alkaline nitrate, the affinity of the nitric acid for the alkali, being = 5, is overcome by that of the 2 atoms of sulphuric acid for the alkali which = 6 + 2 = 8, and the whole of the nitric acid is set free while an alkaline bisulphate is produced (*Sch.* 89).—Similar relations are exhibited by hydrochloric acid towards the sulphates of ammonia, potash, and soda, and by sulphuric acid towards sal-ammoniac and the chlorides of potassium and sodium (Richter, *Stöchiometrie*, 2, 237).

2. *Predisposing affinity of the solvent.* Aqueous acetic acid added to carbonate of potash disengages carbonic acid and forms acetate of potash. But if the solution be evaporated to dryness, the remaining acetate of potash dissolved in alcohol, and carbonic acid gas passed through the solution, almost all the potash is thrown down in the form of carbonate, and the liquid contains acetic acid in combination with alcohol partly converted into acetic ether (Pelouze). It would appear from this that alcohol has a considerable affinity for acetic acid, which affinity together with that of carbonic acid for potash overcomes the greater affinity of acetic acid for potash. This result is usually explained according to Berthollet's theory, the more insoluble and coherent compounds being supposed to be most easily formed, and accordingly in this case, the carbonate of potash which is insoluble in alcohol. This theory is generally resorted to when it directly applies and passed over in silence in cases which contradict it. Why does not carbonic acid throw down carbonate of lime from acetate of lime dissolved in water, inasmuch as carbonate of lime is still less soluble in water than carbonate of potash is in alcohol? Moreover, according to Pelouze, carbonic acid does not decompose chloride of strontium, chloride of calcium, or nitrate of copper dissolved in alcohol, although the carbonates of strontia, lime, and oxide of copper are insoluble in alcohol as well as in water. This instance likewise shows that difficult solubility and great cohesion are two different things; otherwise carbonate of potash would be at the same time a very coherent salt (in relation to alcohol) and a very incoherent one (in relation to water).—The assertion of Berthollet (*Statique Chim.* 1, 401) that a moderately dilute solution of chloride of calcium in water, deposites sulphate of lime when mixed with sulphurous acid and afterwards with alcohol, is one which I have not found to be confirmed. Even a solution of chloride of calcium in absolute alcohol is not rendered turbid by saturation with sulphurous acid gas. (Gm.)

A solution of chloride of sodium and sulphate of magnesia when evaporated to a gentle heat, deposits both salts in crystals without alteration. But if the residue be pulverized and boiled in alcohol, the alcohol according to Grotthus (*Scher. N. Bl.* 273) takes up chloride of magnesium, and the residue therefore contains sulphate of soda (*Sch.* 90). The boiling must however be continued for a long time, and the quantity of chloride of magnesium obtained is very small (H. Rose). Since alcohol dissolves chloride of sodium and sulphate of magnesia very sparingly, but chloride of magnesium very abundantly, the formation of the last-named salt may be due to the predisposing affinity of the alcohol for it; but the

higher temperature produced by boiling with alcohol may also contribute towards the result.

While sulphate of soda and chloride of calcium dissolved in water are resolved by mutual decomposition into chloride of sodium and precipitated sulphate of lime, an aqueous solution of common salt and sulphate of lime evaporated to dryness, or a pulverized mixture of the two salts moistened with a large quantity of water and then dried, yields chloride of calcium when digested in boiling alcohol, while sulphate of soda may be extracted from the residue by water. (*Sch* 90, substituting Ca for Mg.) Unless the mixture of the two salts be moistened with water and then dried, no chloride of calcium will be extracted from it by alcohol (Döbereiner, *J. pr. Chem.* 1, 112). The reversing of the affinity is perhaps produced by the alcohol: possibly however, as Döbereiner supposes, the affinity of sulphate of lime for sulphate of soda (a combination of the two salts occurs in nature forming the mineral called Glauberite,) may cause the formation of a small quantity of the double salt. By melting the two salts together in equal numbers of atoms, we obtain a hard mass, which becomes soft and afterwards moist by exposure to the air, and consequently contains a small quantity of chloride of calcium. These two facts serve to show how it happens that in analyses of mineral waters, when the residue after evaporation is boiled in alcohol, chloride of magnesium or chloride of calcium and sulphate of soda are frequently obtained, though these substances undoubtedly existed in the water as sulphate of lime or magnesia and chloride of sodium.

If 1 part of carbonate of potash be dissolved in at least 10 parts of water, and the solution shaken up with lime, the carbonic acid is taken up by the lime: with 4 parts of water however no decomposition takes place: on the contrary, a strong solution of caustic potash takes carbonic acid from carbonate of lime (Liebig, *Pogg.* 24, 365). The affinity of potash for carbonic acid is probably greater than that of lime; but when the quantity of water is increased, the affinity of that liquid for potash perhaps increases more rapidly than its affinity for carbonate of potash, and thus the first-mentioned result is brought about.

Aqueous sulphurous acid dissolves iodine, forming a mixture of sulphuric and hydriodic acids; but if the quantity of water in the solution be diminished by evaporation, sulphurous acid is evolved and hydriodic acid containing iodine in solution is left behind. Similarly, concentrated sulphuric acid and hydriodic acid are resolved into sulphurous acid and iodine (*Sch.* 91). Hence the affinity of water for sulphuric and hydriodic acids gives rise to their formation.

The following experiment of Chevreul also shows the influence of the solvent. Excess of water abstracts half the potash from neutral stearate of potash, and forms bi-stearate of potash. Ether dissolves stearic acid from neutral stearate of potash, and separates a compound of stearic acid with excess of potash. Water has a more especial affinity for potash, and ether for stearic acid.

3. *Difference of temperature* may give rise to reciprocal affinity in two ways:

a. At high temperatures, the affinity of heat for that substance simple or compound which is most disposed to form a gaseous compound with it, often comes into play and determines the result. Heat, in such cases, acts like a fourth body introduced.

Peroxide of manganese mixed with hydrochloric acid at ordinary or slightly elevated temperatures, gives up its second atom of oxygen to the

hydrogen of the acid, so that water, chlorine, and chloride of manganese or hydrochlorate of protoxide of manganese are produced. (*Sch.* 64, 73.) If on the other hand chlorine gas be exposed to light or to a red heat in contact with water, hydrochloric acid is formed and oxygen gas evolved. At one time therefore oxygen (in peroxide of manganese) takes hydrogen from hydrochloric acid, setting chlorine free; at another, chlorine takes hydrogen from water and evolves oxygen gas. We may with probability suppose that the affinity of oxygen for hydrogen is greater than that of chlorine; on this hypothesis the explanation of the first case is evident. On the other hand, heat has a greater affinity for oxygen than for chlorine; for chlorine gas has been liquefied by strong pressure,—which oxygen has not. When therefore heat acts with great intensity, its affinity for oxygen + that of chlorine for hydrogen effects the decomposition of water.

Potassium at a red heat decomposes black oxide of iron forming potash and metallic iron: at a white heat on the contrary potash is decomposed by metallic iron, the products being black oxide of iron and vapour of potassium. In this case it must be supposed that the affinity of potassium for oxygen is greater than that of iron; nevertheless, at a white heat the affinity of heat for potassium, with which it combines and forms a vapour, comes into play and determines the result.

At a red heat potassium decomposes carbonic oxide, forming potash and charcoal; at a low white heat charcoal decomposes potash, producing carbonic oxide gas and potassium vapour. (*Sch.* 6, *substituting* K for Zn.) In the latter case, the weaker affinity of carbon for oxygen is assisted by that of heat for carbonic oxide and potassium.

When potash (or soda) is in combination with phosphoric acid, boracic acid, or silica, sulphuric acid will separate these substances at ordinary temperatures and combine with the potash by virtue of its greater affinity. If on the contrary sulphate of potash be ignited in contact with phosphoric acid, boracic acid, or silica, these acids will take hold of the potash and separate the sulphuric acid in the state of vapour. In this case it is the affinity of heat for the volatile sulphuric acid, with which it forms a vapour, that enables the much weaker affinity of the above-mentioned acids for potash to gain the mastery.

When carbonate of ammonia is added to an aqueous solution of nitrate of lime, nitrate of ammonia and precipitated carbonate of lime are formed. But when a mixture of nitrate of ammonia and carbonate of lime is heated above 100° C. carbonate of ammonia volatilizes and nitrate of lime remains. (*Sch.* 92.) Here the result is determined by the affinity of heat for the volatile carbonate of ammonia. Similar relations are exhibited between carbonate of ammonia and chloride of calcium in the cold, and between sal-ammoniac and carbonate of lime at a higher temperature. For a similar reason, borate of ammonia and common salt act upon each other only at a high temperature, evolving sal-ammoniac in the state of vapour.

To the same category may also be assigned the following facts, so far as they may prove to be correct. When sulphuric acid acts upon zinc under the ordinary pressure of the atmosphere, sulphate of zinc and hydrogen gas are evolved (*Sch.* 17); but according to Babinet (*Ann. Chim. Phys.* 37, 183; also *Pogg.* 12, 523) this decomposition ceases when the process is conducted in a strong copper vessel closed by a stop cock, as soon as the disengaged hydrogen gas has attained a certain pressure; at 10° C. the decomposition and evolution of gas cease when the gas presses with a force of 13 atmospheres; at 25°, when the pressure amounts to 33

atmospheres. This seems to show that the affinity of zinc for oxygen + that of sulphuric acid for oxide of zinc is less than the affinity of hydrogen for oxygen — that of sulphuric acid for water, and therefore the decomposition does not take place under strong pressure;—but at lower pressures, when the affinity of heat for hydrogen, with which it forms a gas, likewise comes into play, the action goes on. On the contrary, Faraday has observed (*Qu. J. of Sc.* 3, 474) that at this increased pressure, the decomposition is not arrested but merely retarded, because the effervescence ceases and with it the motion of the liquid, by which the chemical action is materially assisted. I have also obtained the following results at a summer heat of from 20° to 30° C. (68° to 86° Fah.), using very thick and narrow glass tubes 5 inches in length. On filling the tube $\frac{2}{3}$ full of moderately strong hydrochloric acid, introducing a piece of zinc just above the acid, sealing the tube, and laying it in a horizontal position, it burst after four hours with a violent explosion. Now since a tube of equal strength is capable of holding liquid carbonic acid at 25° C. without bursting, and the elasticity of carbonic acid at that temperature amounts to 50 atmospheres, that of the hydrogen gas in the experiment just described must have exceeded 50 atmospheres. When a similar experiment is made with a mixture of 1 part of oil of vitriol and 8 of water, the tube does not burst even when left in the horizontal position for several weeks and placed upright every day. On cutting off the end, the gas escapes with a slight detonation without bursting the tube, and the acid is found to be nearly saturated with zinc. This seems to show that the decomposition is not arrested by strong pressure but only retarded.

The following experiment (recorded in Berzelius's *Lehrbuch*, 5, 9) is also connected with this matter. When pieces of carbonate of lime are placed in a strong glass vessel, a somewhat dilute acid poured upon them, and the vessel closed air-tight, the solution ceases after a time, and the lime is no longer attacked for whatever length of time it may be left in the acid; but on opening the vessel the lime is in a few minutes completely dissolved. From this it might be inferred that the affinity of carbonic acid for lime is greater than that of sulphuric, nitric, or hydrochloric acid, that these acids decompose carbonate of lime only under comparatively small pressure, when the action is assisted by the affinity of heat for carbonic acid with which it forms a gas,—that at strong pressures, on the contrary, carbonic acid would expel these acids from their combinations with lime. (*Sch.* 12.) But hydrochloric acid of moderate strength exhibits a different relation from this, at least according to my experiments. A quantity of acid like that above mentioned having been sealed up in a tube together with an excess of calcspar, the tube laid horizontally but turned upright every day in order to renew the points of contact, the liquid was found after 14 days to be covered with a highly moveable film of liquid carbonic acid, 2 lines in thickness. On cutting off the point, the upper half of the tube burst with a loud report, and the remaining liquid was neutral to litmus-paper. This experiment shows that hydrochloric acid decomposes carbonate of lime even under a pressure at which carbonic acid becomes liquid, and therefore that the affinity of hydrochloric acid for lime is greater than that of carbonic acid.

Lastly, with reference to this subject, we may mention an experiment of Petzhold (*J. pr. Chem.* 17, 464), according to which pulverized quartz heated to whiteness in an open vessel with an equal weight of carbonate

of lime expels the carbonic acid, but produces no such effect when the mixture is heated in a strong closed iron vessel. In this case, it may with great probability be supposed that the affinity of silica for lime is weaker than that of carbonic acid, and that the formation of silicate of lime takes place only when the action is assisted by the affinity of heat for carbonic acid.

b. In other cases, difference of temperature appears to modify the result in consequence of the cohesion (or affinity?) of bodies increasing and diminishing in different degrees at lower and higher temperatures,—and here in particular Berthollet's law regarding the decomposition of salts by double affinity finds its application.

A solution of common salt and sulphate of magnesia evaporated at ordinary temperatures, or a little above, allows both salts to crystallize out unaltered (page 127); but at 0° C, or at lower temperatures, as was long ago observed by Scheele, hydrated sulphate of soda crystallizes out and the solution retains chloride of magnesium; on gently warming the whole, common salt and sulphate of magnesia are again obtained. But above 50° C. (122° Fah.) the solution again deposits sulphate of soda, though in the anhydrous state. (H. Rose, *Pogg.* 35, 180.) These results may be explained by the different solubility of sulphate of soda at different temperatures: at 0° C. one part of sulphate of soda requires 8·2 parts of water to dissolve it, at 33° the smallest quantity, viz. 0·33, and at 50·4° again 0·38 parts. Below 0° and above 50° the solubility must be considerably less. Since now, according to Berthollet's law, the least soluble salt is always produced, sulphate of soda separates both below 0° and above 50°, because at these extremes of temperature its solubility is less than that of common salt or sulphate of magnesia; at medium temperatures, on the contrary, at which sulphate of soda is more soluble than common salt or sulphate of magnesia, these salts remain unaltered.

In a similar manner, sulphate of soda and chloride of potassium dissolved together in water resolve themselves, at ordinary temperatures, into sulphate of potash and chloride of sodium, whereas, according to Hahnemann and Richter (*Stöch.* 2, 224) a solution of the last-named salts at −20° C (−4° Fah.) deposits sulphate of soda. At ordinary temperatures sulphate of potash, at low temperatures sulphate of soda is the less soluble salt. According to Constantini, alum and common salt yield crystals of Glauber's salt at freezing temperatures, and according to Hahnemann, Glauber's salt crystallizes at very low temperatures, even from a mixture of saturated solutions of gypsum and common salt.

The explanation of the following cases—by supposing a disproportionate alteration of cohesion to be produced by change of temperature—is not quite so satisfactory.

An aqueous solution of sulphate of lime gives with chloride of barium a precipitate of sulphate of baryta, while chloride of calcium remains in solution. (*Sch.* 52.) If, on the other hand, chloride of calcium be fused with sulphate of baryta, a mixture of sulphate of lime and chloride of barium is formed, the latter of which may be removed by rapidly boiling the powdered mass in water and filtering; but by longer standing under water the whole would again be converted into sulphate of baryta and chloride of calcium. Does the affinity of water for chloride of calcium contribute to this result?

Sulphate of baryta is decomposed both by fusion with carbonate of soda and by boiling with the aqueous solution of that salt (though but imperfectly), yielding carbonate of baryta and sulphate of soda; on the

contrary, as Kölreuter has shown, carbonate of baryta is decomposed by digestion with sulphate of soda at ordinary temperatures, the products being sulphate of baryta and carbonate of soda.

A dilute solution of nitrate of lime remains clear when mixed with a solution of sulphate of soda, but deposits sulphate of lime when warmed. (Persoz.)

A solution of alum does not become turbid when mixed with very small quantities of carbonate of lime or soda, but on evaporation at a gentle heat, yields crystals of cubic alum. But when more strongly heated, the solution becomes turbid and deposits basic sulphate of alumina which redissolves as the solution cools.

A solution of pure acetate of alumina does not become turbid on heating, but undergoes that change if it contains sulphate of ammonia, potash, soda, or magnesia; a fainter turbidity is produced by the addition of nitrate of potash, none by the addition of nitrate or acetate of baryta, chloride of calcium, or acetate of lead. The precipitate which consists of hydrate of alumina disappears when the solution is cooled, and appears again on heating. (Gay-Lussac, *Ann. Chim.* 74, 193, also *Schw.* 5, 49; further, *Ann. Chim. Phys.* 6, 201, also *Schw.* 21, 96.)

Persulphate of iron mixed with acetate of potash deposits hydrated peroxide of iron on boiling.

An aqueous mixture of borate of soda and sulphate of magnesia yields, on application of heat, a precipitate of borate of magnesia, which however disappears each time on cooling.

Metallic silver takes oxygen from persulphate of iron dissolved in water, when boiled in the liquid, so that a solution is formed containing sulphate of silver and protosulphate of iron; but on cooling, all the silver is reprecipitated in the metallic state, and the solution once more contains sulphate of peroxide of iron. (*Sch.* 94.)

In many other cases the occurrence of reciprocal affinity is only apparent.

When ammonia is added to neutral sulphate (nitrate or hydrochlorate) of magnesia, it is taken up and magnesia precipitated; on the other hand, magnesia expels ammonia from the neutral sulphate (nitrate or hydrochlorate) of ammonia and is itself dissolved. In both cases however the decomposition is only half complete, in whatever excess the ammonia or magnesia may be added. In the first case, half of the sulphate of magnesia remains undecomposed and unites with the sulphate of ammonia in the form of a double salt containing 2 atoms of sulphuric acid, 1 atom of ammonia, and 1 atom of magnesia; in the second, half of the ammoniacal salt remains undecomposed, and forms the same double salt with the sulphate of magnesia produced. (*Sch.* 95 and 96.)

Nitric acid added to chloride of potassium forms nitrate of potash, and sets hydrochloric acid free; on the other hand, nitrate of potash is converted by excess of hydrochloric acid into chloride of potassium. The affinity of potassium for oxygen + that of chlorine for hydrogen + that of nitric acid for potash is undoubtedly greater than the affinity of potassium for chlorine + that of hydrogen for oxygen; and thus the first case explains itself. (*Sch.* 97.) If, on the contrary, nitrate of potash is to be converted by hydrochloric acid into chloride of potassium, a great excess of the acid must be used and heat be applied: moreover the excess of hydrochloric acid does not expel the nitric acid in i tered state, but the two together are resolved into hyponitric a i, chlorine, and water. (*Sch.* 98.) Thus it is not nitric acid bu weaker hypo-

nitric acid that is driven out by the hydrochloric acid. Nitric acid separates arsenious acid from an aqueous solution of arsenite of potash; but when nitrate of potash is ignited in contact with arsenious acid, nitrous acid is evolved and arseniate of potash formed. In this case, the stronger nitric acid is converted by loss of oxygen into the weaker nitrous acid, while on the contrary, the weaker arsenious acid is by access of oxygen converted into the stronger arsenic acid. The affinity of arsenious acid for oxygen + that of arsenic acid for potash overcomes the affinity of nitrous acid for oxygen + that of nitric acid for potash. (*Sch.* 99.)

The existence of reciprocal affinity has also been inferred from the fact that certain salts, which when dissolved in a small quantity of water decompose one another by double affinity, producing a precipitate of a difficultly soluble salt, give no precipitate in more dilute solutions,—although the quantity of water present would not be sufficient to hold in solution the less soluble salt which may be produced by the decomposition, if it existed in the separate state. For example, sulphate of lime requires about 400 parts of water to dissolve it; but chloride of calcium, dissolved in about 200 parts of water (which would produce more than an equal quantity of sulphate of lime) gives no precipitate with sulphate of potash. Many chemists conclude from this that when this large quantity of water is present, the chloride of calcium is not decomposed by the sulphate of potash, since if sulphate of lime were formed, more than half of it would be precipitated. But it is simpler to suppose that the formation of sulphate of lime takes place even in this case, but that the presence of the chloride of potassium, which is formed at the same time, renders it more soluble than it otherwise would be. Similarly, it was long since observed by Guyton-Morveau that lime-water rendered turbid by passing carbonic acid gas through it becomes clear again on the addition of sulphate of potash or chloride of potassium, as if the presence of these salts rendered the carbonate of lime more soluble: and Karsten (*Schrift. d. Berl. Akad.*, 1841) has shown that many easily soluble salts are rendered more soluble by the addition of other salts. These mutual affinities of salts, and the greater solubility in water thereby produced, explain the occurrence of carbonate and sulphate of lime, carbonate of magnesia, &c., in mineral waters, in quantities greater than pure water could dissolve; so that this phenomenon by no means renders it necessary to suppose that such waters contain salts which are incompatible with each other, *i. e.*, which at the given temperature would decompose one another and form a precipitate, if the quantity of water present were smaller. *Comp.* Berthollet (*Statique Chim.*, 1, 103, and 129); Brandes (*Schw.* 43. 153; 46, 433.)

Many other facts relating to the theory of reciprocal affinity but requiring more accurate investigation may be found in Scheele (*Opusc.* 1, 223): Grotthuss (*Scher. N. Bl.* 275): N. Fischer (*Pogg.* 7, 263): Berthollet (*Statique Chim.* 1, 81, 99, 100, 401) and Dulong (*Ann. Chim.* 82, 273, also *Schw.* 5, 369). In the experiments of the last-named philosopher on the decomposition of insoluble by soluble salts, variation of temperature, which might have produced opposite results, does not seem to have been sufficiently attended to.

2. *Circumstances and Results of Decomposition.*

a. Change of temperature. Since heat is generally set free in the combination of bodies, an equal quantity of heat must also become latent

at their decomposition. Nevertheless most decompositions are accompanied by rise of temperature sometimes amounting to the most vivid combustion. With reference to this matter the following cases must be distinguished:—

a. When peroxide of hydrogen is decomposed by heat or by the contact of pulverized bodies into water and oxygen gas, a great deal of heat and even light is developed, notwithstanding that a considerable quantity must be rendered latent in the formation of the gas. This remarkable instance leads us to suppose that in the formation of this very loosely united compound heat is not set free but rendered latent, that in fact oxygen gas + heat enters into combination with the water.—A similar constitution may exist in certain metallic bromates which when heated are resolved with sudden incandescence into a metallic bromide and oxygen.

β. When bodies separate in the solid form from their solution in a liquid or a gas, in consequence of their cohesion being increased by cooling, a development of heat takes place, the heat of fluidity which the bodies had previously absorbed in the act of solution being set free.

γ. Most decompositions take place in consequence of weaker affinities being overcome by stronger ones. Now even if heat be rendered latent by the destruction of the compounds produced by the weaker quiescent affinities, a still greater quantity must nevertheless be set free in consequence of the neutralization of the stronger decomposing affinities, and the rise of temperature attending the decomposition marks the difference between these two quantities of heat.—If A develope a quantity of heat $= 2$ in combining with B, and $= 3$ in combining with C, then in the decomposition of A B and formation of A C, a quantity of heat must be developed $= 3 - 2 = 1$.

Lowering of Temperature takes place when gaseous products of decomposition are evolved from solid or liquid compounds, and the absorption of heat thereby produced is not compensated by a development of heat resulting from the formation of new compounds.—The escape of carbonic acid gas from water charged with it, on diminishing the pressure, is accompanied by diminution of temperature; on the contrary, when this gas is disengaged from a solution of carbonate of soda by the addition of sulphuric acid, a slight rise of temperature is produced.

[On the development of Electricity by chemical decomposition, vid. *Electricity.*]

b. The time in which decomposition takes place depends chiefly on the circumstances noticed on page 39. If one of the products of decomposition is gaseous and has to make its escape from a liquid, the decomposition is accelerated by the presence of angular bodies.

c. Qualitative alteration. Every decomposition results in the production of at least two heterogeneous substances or products of decomposition, which may be either solid, liquid or gaseous, and—so long as they do not separate by virtue of their different specific gravities—produce a cloudy, opaque mixture.

If the decomposition is attended with the formation of gaseous products, effervescence and explosion may ensue.—*Effervescence* or *frothing* is produced when a gaseous body is continually developed and rises up in bubbles during the decomposition of a liquid;—Carbonate of potash and sulphuric acid.

In *Explosion, Detonation* (or *Puffing*, when [illegible] is fainter) a gaseous product of decomposition (or several) is [illegible] almost instantly

from a solid (*e. g.* fulminating silver), a liquid (chloride of nitrogen) or a gas (oxide of chlorine)—and in endeavouring to expand itself into the much larger volume corresponding to its elasticity (often greatly increased by rise of temperature) forcibly presses back the air and other objects, producing detonation and breaking the solid bodies in its neighbourhood.—Even gaseous compounds, such as oxide of chlorine, may be decomposed with explosion, if the separated elements, such as chlorine and oxygen gases, take up a larger volume than that occupied by the compound.—The production of light which accompanies so many of these explosions often proceeds from this circumstance,—that great heat is developed in the decomposition in consequence of the formation of more intimate compounds, as in the explosion of gunpowder, detonating powder, &c. and this higher temperature imparts to the gases and vapours at the moment of their production a proportionately increased elasticity, and thereby strengthens the explosion. In the decomposition of oxide of chlorine, chloride of nitrogen, iodide of nitrogen, &c., which appears not to be attended with a rise of temperature amounting to ignition, the development of light may perhaps be explained by the violent compression of the air around the exploding body.—The theory of the detonation of an explosive mixture propounded by Brianchon (*Bibl. univ.* 28, 393) has been shown by Gay-Lussac (*Ann. Chim. Phys.* 29, 53) to be untenable. R. Böttger has also shown (*Ann. Pharm.* 29, 75) that the explosive force of fulminating silver is equally strong in all directions.

When several *liquid products* result from a decomposition, they form a turbid mixture, until they have taken up the determinate relative positions corresponding to their different specific gravities:—Volatile oil dissolved in alcohol with water.

When in the decomposition of a liquid or gaseous body, *solid products* are formed and sink to the bottom in consequence of their greater specific gravity, they are called *Precipitates*, and a decomposition of this kind is called *Precipitation*,—*Spontaneous Precipitation*, (*Præcipitatio spontanea*) when the separation of the solid body takes place merely from change of temperature (page 113);—*Forced Precipitation*, (*Præcipitatio coacta*) when it is brought about by the addition of another ponderable body, the *Precipitant* (*Præcipitans*). If the solid product of decomposition is specifically lighter than the liquid, it is separated as a *Scum* (*Cremor*).—The precipitate and the scum may be either educts or products.—Lime precipitate from lime-water by alcohol is an educt; oxalate of lime precipitated from lime-water by oxalic acid is a product.

The atoms of the solid product of decomposition unite themselves at the moment of their separation or formation into larger masses, which however possess various magnitudes and forms depending chiefly on the nature of the bodies, so that to a certain extent the nature of the precipitate may be inferred from its outward appearance: considerable influence is however exerted by the time in which the precipitation takes place and the degree of dilution of the liquid. The following forms of precipitates may be particularly distinguished,—and of these the first two must be regarded as anarphous, the others as crystalline: *Flocculent;* aggregation in large, loose, threadlike masses: alumina, hydrated peroxide of iron, phosphate of lime.—*Curdy;* in this form the masses are still larger and more dense and solid, but still uncrystalline: chloride of silver as it is precipitated from solutions of silver-salts by hydrochloric acid; casein as precipitated from milk by an acid.—*Pulverulent;* the atoms are united in small, imperfectly crystalline masses: sulphate of baryta as precipitated

by sulphuric acid from solutions of baryta-salts; silver as precipitated by proto-sulphate of iron from nitrate of silver.—*Granular;* coarsely pulverulent masses having a more distinct crystalline character: sulphate of potash as precipitated by sulphuric acid from aqueous solution of carbonate of potash.—*Arborescent;* the union of a great number of individual crystals into larger ramified masses: *metallic trees.*

V. Magnitude or Strengh of Affinity.

There must exist a relation inexpressible in numbers between the magnitude of chemical affinities and those of other natural forces, such as gravitation, adhesion, or cohesion.

Absolute strength of affinity.—A solution of nitre saturated while warm deposits part of the nitre at 0° on account of increasing cohesion. Now supposing we were to determine what suspended weight would be required to break a crystal of nitre of a given thickness at 0°; then this weight would express the affinity of the water saturated with nitre at 0° for more nitre: for after the crystallization at 0° has ceased, this affinity is in equilibrio with the cohesion. A similar process might be adopted with other bodies soluble in water, the cohesion being always determined with reference to a crystal of given thickness. On the same principle Lavoisier and Laplace proposed to bring an acid of various degrees of strength into contact with ice at different temperatures below 0°, and to enquire at what degree of cold and at what dilution the acid ceased to exert any solvent power on the ice, and consequently its affinity for the ice became exactly equal in force to the cohesion of that substance—and thus to reduce the affinity of the acid for the ice, at different states of concentration, to degrees of the thermometer. A similar method might be adopted with various salts and ice: since for example common salt ceases to act on ice at −20° C., but chloride of calcium not till −60°, the affinity of the latter for water must be much greater than that of the former. But these methods only enable us to determine the weights or degrees of temperature by which the weakest and least important affinities may be expressed. All affinities which have any considerable value exceed the force of cohesion to such a degree, that comparison between the two powers becomes impossible.

For the present we must content ourselves with an approximate determination of *relative strength of affinity, i. e.,* of the proportion which individual magnitudes of affinity bear to one another without reference to other natural forces. Perhaps we shall some day be able to affix a certain relative number to each particular magnitude of affinity; at present, however, we are contented if we can determine, with some degree of certainty, in what order the affinities of different bodies for a given body succeed one another with regard to their strength.

Is the affinity between two bodies different at different temperatures? Just as heat weakens cohesion by striving to increase the distance between homogeneous atoms, so likewise it may diminish the strength of affinity by increasing the difference between heterogeneous atoms. It appears, however, that as long as the action of heat does not go so far as to form a gaseous compound with one of the bodies, —in which case it would act like a third ponderable body in undoing the combination,—it does not weaken chemical attraction, probably because in a combination of two ponderable bodies, it tends to increase the distance of the compound atoms only, not of the simple ones by whose

union the compound atoms are formed. On the other hand, it might be inferred, from the phenomena mentioned on page 36 D, that elevation of temperature increases the strength of affinity. When, for example, sulphur combines with carbon at a red heat, we might suppose that the affinity between the two bodies is called into action by this temperature, or at least heightened in such a degree as to be able to overcome the cohesion of carbon; but in that case the sulphuret of carbon ought, on cooling, when the affinity is again diminished or annihilated and the cohesion of the carbon increased, to be again resolved into its elements. Such, however, is not the case either with this or with any other of the more intimate compounds, and therefore the affinity between such bodies exists even in the cold,—and heat does not develope affinity in the first instance, but favours the exertion of it in a manner not hitherto explained. At present, therefore, there is no ground for supposing that the affinity between two bodies is different at different temperatures. If, indeed, we would explain Berthollet's law of double affinity, not by the influence of cohesion, but on the supposition that out of a number of possible compounds those actually formed are always the most intimate, and have likewise the smallest relative solubility (page 125), it might, perhaps, be necessary to assume, with reference to the reciprocal affinity between common salt and sulphate of magnesia, for example (page 127), that the magnitudes of the affinities are different at different temperatures.

The following are the principal methods which have been adopted for the determination of relative magnitudes of affinity.

A. Difference of magnitude or strength of affinity is determined by the results of conflict or opposition of affinities, on the principle that the decomposing must be stronger than the existing or quiescent affinities.

a. Decompositions in which the Affinity of Heat contributes to the Result.

Many combinations of ponderable substances are decomposed by elevation of temperature, one of the ponderable elements combining with heat and forming a gaseous compound. The affinity of heat for ponderable bodies must be supposed to increase with the quantity in which it is accumulated, and therefore with the temperature; consequently, the temperature required to decompose a compound of a less volatile with a more volatile body will increase with the affinity between the two. According to this, the strength or magnitude of the affinity may perhaps be found from the temperature required to effect the decomposition;—the boiling point of the more volatile element must, however, be likewise taken into consideration.

Iron pyrites, FeS^2, when raised to a moderate red heat, which may be estimated at about 500° C., gives off vapour of sulphur, and is converted into Fe^7S^8; at a stronger red heat (perhaps = 800°), a still greater quantity of sulphur sublimes, and Fe S remains behind. Taking Dumas' determination of the boiling point of sulphur, viz., 440°, and supposing the higher degrees of temperature (a more accurate determination of which would, however, be desirable) to be correct, the affinity of Fe S for the quantity of sulphur required to produce Fe^7S^8, may be expressed by 800 − 440 = 360, and that of Fe^7S^8 for as much sulphur as will produce FeS^2, by 500 − 440 = 60. Sulphuret of gold, AuS^3, parts with all its sulphur, perhaps at about 450°; if so, the affinity of gold for sulphur will be expressed by 450 − 440 = 10. But few of the other metallic sulphurets are decomposed by heat; whence we may conclude that the number which would express the affinity of these metals for sulphur is

greater than the number of degrees of temperature which the sulphurets can bear without decomposition, *minus* 440°. In a similar manner might be determined the affinity of iodine, bromine, and chlorine for the few metals from which they can be separated by heat, provided the temperatures at which the decompositions take place could be more accurately determined: so likewise might be estimated the affinity of mercury and arsenic for certain other metals, that of ammonia for the more fixed acids, such as the boracic and phosphoric acids, and that of carbonic acid for most salifiable bases. The greater number of bases part with their combined carbonic acid at a low red heat, lime at a somewhat higher temperature, strontia at a still higher, baryta only in the strongest wind-furnace, potash and soda not at all. Accordingly, the last two bases must have the strongest affinity for carbonic acid; and the fact of lime, baryta, and strontia taking carbonic acid from them when a considerable quantity of water is present, must be explained by the greater affinity of water for caustic potash and soda (page 128). Nitrate of copper is decomposed at a lower heat than nitrate of silver, whence it follows that the latter oxide has the greater affinity for nitric acid. Lastly, since many oxidized compounds, such as peroxide of manganese, chromic acid, antimonic acid, and arsenic acid give up part of their oxygen at a high temperature, and the noble metals give up the whole of it, and since the compounds of hydrogen with carbon, phosphorus, and sulphur, and those of nitrogen with chlorine and iodine are decomposed at various temperatures,—the affinities by which these compounds are held together may be at least comparatively determined;—but no exact numbers can be assigned to them, because the boiling points of oxygen, hydrogen, and nitrogen are unknown. This method of determining magnitudes of affinity deserves closer examination.

b. Decompositions in which Ponderable Bodies are alone concerned.

a. By *Simple Affinity.* If we find that the compound A B is decomposed by C with formation of A C, and that similarly the compound A C is decomposed by D with formation of A D, &c., we conclude that A has the greatest affinity for D, the next for C, and the smallest for B. In this manner, A may be tested with respect to all the substances with which it can combine. If, then, we place A at the head, and below it all the substances capable of uniting with it, in the order in which their affinity for A diminishes, we obtain the *Column of Affinity* of A. And if we proceed in the same manner with other bodies, simple and compound, assigning a column to each, and collecting all these columns into a general table, we shall obtain a *Table of Affinity, Tabula Affinitatum.*

The first table, which was very imperfect, was drawn up by Geoffroy; he was followed by Gellert, Rüdiger, Limbourg, Marherr, De Fourcy, Demachy, Erxleben, Weigel, Wiegler, and Bergman.

A few examples will suffice to illustrate this method. Carbonate of lime treated with hydrochloric acid yields hydrochlorate of lime and carbonic acid; hydrochlorate of lime is resolved by sulphuric acid into sulphate of lime and free hydrochloric acid; and when oxalic acid is added to a solution of sulphate of lime in water, oxalate of lime is thrown down, while free sulphuric acid remains in the water. Hence in the column headed *Lime*, the four acids above mentioned succeed one another in the following order: oxalic, sulphuric, hydrochloric, carbonic. From an aqueous solution of sulphate of alumina ammonia precipitates the alumina, producing sulphate of ammonia; this salt is converted by lime into sul-

phate of lime and free ammonia; the sulphate of lime treated with solution of potash is resolved into sulphate of potash and free lime; and, lastly, the aqueous solution of sulphate of potash gives with baryta-water a precipitate of sulphate of baryta, while free potash remains in solution. Consequently in the sulphuric acid column, the four bases here considered would stand in the order: baryta, potash, lime, ammonia, alumina.

Simple and sure as this method may appear, and well as it may be adapted to furnish available materials for the determination of relative magnitudes of affinity, it is still far from being unexceptionable, and demands the greatest caution in its application. The influence of cohesion, elasticity, and the affinity of the solvent, are especially deserving of the most careful attention. For example, that oxalic acid added to an aqueous solution of sulphate of lime precipitates oxalate of lime, might be explained on the hypothesis that the cohesion of the latter salt is greater than that of the former; and that at the same time the affinity of water for sulphuric acid is greater than for oxalic acid; if such be the case, the affinity of sulphuric acid for lime may still be greater than that of oxalic acid. It has also been suggested that hydrochloric acid may expel carbonic acid from carbonate of lime, not in consequence of greater affinity, but because carbonic acid is more elastic *i. e.*, has greater affinity for heat than hydrochloric acid has; but this supposition is negatived by the experiment described on page 130, in which the decomposition was found to take place under a pressure sufficient to liquify the carbonic acid set free. Again it has been shown (p. 129) that *e. g.*, boracic acid decomposes sulphate of soda at a red heat, whilst the opposite effect takes place in the cold. Generally, the various cases of reciprocal affinity (page 125 . . . . 133) show that it is important to examine the action of bodies under variously altered circumstances, and in drawing conclusions respecting magnitude of affinity from decompositions which result from simple affinity, never to neglect the circumstances which, as was shown in discussing the theory of reciprocal affinity, may invert the result and enable the weaker affinity to gain the victory. One of these circumstances, viz., difference of temperature, was long ago noticed by Bergman. In his table, the *Affinitates electivæ via humida* are distinguished from those *via sicca*, accordingly as the decompositions take place at ordinary temperatures or at a red heat. This mode of distinction is not indeed unexceptionable, since opposite results often take place at different degrees of incandescence: thus, for example, at a red heat potassium takes oxygen from iron, while at a white heat iron takes oxygen from potassium. At the same time such distinctions oblige us to admit that tables of affinity do not always give the relative magnitudes of that force, but merely the results of decomposition under certain circumstances: hence these tables are by many chemists called *Tables of Precipitation*, or more correctly, *Tables of Decomposition*.

It must also not be forgotten that a body C sometimes takes from the body B only a part of the body A. When soda precipitates oxide of lead from a solution of chloride of lead in water—which may be regarded as hydrochlorate of oxide of lead—this does not exactly prove that the affinity of soda for hydrochloric acid is greater than that of oxide of lead; for the precipitate is a compound of 4 atoms of oxide of lead with one atom of hydrochloric acid; and the same compound is on the other hand produced, with separation of soda, when oxide of lead in excess is digested with a solution of hydrochlorate of soda. From this it follows that 4 atoms of oxide of lead have a greater affinity for 1 atom of hydro-

chloric acid than 1 atom of soda has; but that 1 atom of soda has a greater affinity for hydrochloric acid than 1 atom of oxide of lead, and consequently abstracts from the latter $\frac{3}{4}$ of the acid with which it is combined. Hence, in precipitations of this kind, it must be carefully examined whether the precipitate contains the substance B in a state of purity or still in combination with part of the body A.

Lastly, on bringing together A B and C, we very often obtain, not A C and B, but A C and B C. If, for example, in order to determine whether arsenic or sulphur has the greater affinity for oxygen, we heat together arsenious acid and sulphur, we obtain indeed sulphurous acid, but the separated arsenic combines with another portion of the sulphur and forms sulphuret of arsenic (*Sch.* 100). In this case we cannot conclude that oxygen has a greater affinity for sulphur than for arsenic, but only that the affinity of sulphur for oxygen + that of sulphur for arsenic is greater than that of arsenic for oxygen;—the affinity of heat for sulphurous acid must likewise be taken into account.

β. By *Double Affinity.* Guyton-Morveau supposed that when two salts decompose one another, the sum of the two decomposing affinities must be greater than that of the two quiescent affinities. According to the decompositions which the salts of certain acids and bases exhibit one with another, he endeavoured to assign such magnitudes to their affinities that calculation should agree with observed results. He thus found by trial the following numbers:—

	Sulphuric Acid.	Nitric Acid.	Hydrochloric Acid.	Acetic Acid.	Carbonic Acid.
Baryta	66	62	36	28	14
Potash	62	58	32	26	9
Soda	58	50	31	25	8
Lime	54	44	24	19	12
Ammonia	46	38	21	20	4
Magnesia	50	40	22	17	6
Alumina	40	36	18	15	2

According to this table, sulphate of soda and hydrochlorate of baryta must decompose each other, because $66 + 31 (= 97)$ is greater than $58 + 36 (= 94)$; similarly with carbonate of potash and acetate of lime, since $12 + 26 > 19 + 9$, and so on. But in many cases in which decomposition takes place the sums are equal; *e. g.*, with sulphate of potash and nitrate of baryta ($62 + 62 = 66 + 58$); and with sulphate of potash and hydrochlorate of baryta ($62 + 36 = 66 + 32$). In others the sum of the latent is even greater than that of the separating affinities, so that the calculation directly contradicts the experimental result; *e. g.*, in the case of nitrate of baryta and sulphate of soda ($62 + 58 > 50 + 66$); so likewise nitrate of baryta is decomposed by sulphate of ammonia, sulphate of lime, sulphate of magnesia or carbonate of soda, and sulphate of magnesia by carbonate of ammonia, although calculation would lead to the contrary result. Moreover, Guyton-Morveau assigns to the affinity of nitric and hydrochloric acid for baryta larger numbers than to the affinities of the same acids for potash, although potash separates baryta both from the nitrate and hydrochlorate of that base. Generally, it is easy to see that it would be useless trouble to a tify the preceding numbers and adapt them to all decom se salts by

double affinity,—since these results depend, not alone on the sum of the magnitudes of affinity, but also on cohesion, temperature, and the nature of the solvent.

B. Attempts have been made to determine the relative strength of affinity of two bodies from their force of adhesion. Guyton-Morveau regarded adhesion as a commencing affinity; supposing that heterogeneous substances attract each other in masses before the attraction between their individual atoms comes into play and forms chemical compounds. The greater therefore the affinity between two bodies, the greater should also be their adhesion, and the magnitude of the former should also be determinable from that of the latter. Morveau suspended a metal disc one inch in diameter from one of the arms of a balance, and counterpoised it by weights in the opposite scale; he then placed under the disc a glass filled with mercury, so that the surface of the mercury just came in contact with the lower surface of the disc,—and ascertained what additional weight required to be laid in the opposite scale-pan in order to separate the disc from the mercury. In this manner he found that the following weights were necessary: gold 446 grains, silver 429, tin 418, lead 397, bismuth 372, zinc 204, copper 142, antimony 126, iron 115, cobalt 8. This is almost exactly the order of facility in which these metals combine with mercury, and so far experiments appear to accord with the preceding view. But it has not yet been shown that the magnitudes of adhesion and affinity are in direct proportion one to the other. Although the affinity of sulphur for mercury is much greater than that of either of the metals just named, still a disc of sulphur would adhere to it with far less force than either of the metallic discs did. Moreover, the fact of mercury combining with gold more easily than with zinc does not show that gold has the greater affinity for the mercury: for facility of combination is one thing, intimacy another. Besides, Morveau's method does not give even the force of adhesion; for a certain quantity of mercury remains attached to the plates, and on separation the mercury itself is torn asunder, and the force determined is in reality its cohesion. Finally both on this ground, and because many substances on coming in contact immediately enter into chemical combination,—and the film of the new compound of the two bodies whose adhesion is to be measured is really that which suffers disruption,—an exact determination of the force of adhesion in the most numerous and important cases is impossible.

C. The strength of affinity is sometimes estimated by the time in which combination takes place. Wenzel (*Von der Verwandtschaft*, p. 28) exposed metal cylinders of equal height and diameter, and covered all over, with the exception of one of the terminal surfaces, with varnish —to the action of different acids at the same temperature and for equal intervals of time, and estimated the force of affinity by the quantity of metal dissolved. These experiments however prove nothing, first because in the solution of metals in acids various affinities come into play, viz., the affinity of the metal for oxygen, which has to be taken sometimes from the acid sometimes from the water,—that of the oxide of the metal for the acid—and that of the salt for water; secondly, because Wenzel sometimes used concentrated, sometimes dilute acids, according to the condition of the metal—and thirdly, because a given surface of different metals exposes a different number of atoms to the action of a solvent, according to the atomic weights and densities of the metals. But even experiments in which these sources of error were eliminated would lead to nothing, because the important influence which cohesion, specific gravity,

&c. exert on the rapidity of the combination could not well be taken into account.

D. Strength of affinity has been estimated from the quantities in which bodies combine.

Berthollet laid down the following hypothesis: The smaller the quantity of a body B required to neutralize another body A, that is to say to balance its opposite properties, the more completely opposite must B be to A, and the greater must therefore be their mutual attraction. If for example a certain quantity of an acid is neutralized by 1 part of the base B, but requires 2 parts of the base C and 3 of the base D, the affinities of A to B, C, and D = 3 : $1\frac{1}{2}$: 1; in short, the force of affinity is inversely as the quantity required for neutralization. A similar relation exists with regard to the affinity of a base for several acids; that acid of which the smallest quantity suffices for the neutralization of the base, will have, of all acids, the greatest affinity for the base. This view of the matter is contradictory to the order of affinity found from decompositions by double affinity. For example, 40 parts of sulphuric acid are neutralized by 76·6 baryta, 52 strontia, 47·2 potash, 31·2 soda, 28·5 lime, 20·7 magnesia and 17 ammonia; and 28·5 lime are neutralized by 40 sulphuric acid, 54 nitric acid, 36·4 hydrochloric acid, 127 hydriodic acid, 32 sulphurous acid, and 22 carbonic acid. The bodies here follow in the order in which they separate each other, so that for example baryta takes sulphuric acid from all other bases and sulphuric acid takes lime from all other acids. The law here manifested —that, for the most part, those substances of which the smallest quantities are required to neutralize a third body—and which should therefore have the greatest affinity for that body—are separated by those which combine with the same body in greater proportion, and should therefore have less affinity for it—is explained by Berthollet from the influence of cohesion and elasticity. According to that philosopher ammonia has, of all the bases here enumerated, the greatest affinity for sulphuric acid, for it is the base of which the smallest quantity is required to neutralize that acid: that it should however be separated from sulphuric acid by all other bases arises from its tendency to assume the gaseous form. From the same cause the highly elastic substance carbonic acid, which of all acids has the greatest affinity for lime, is separated from that base by hydrochloric acid: (the incorrectness of this explanation is manifest from the experiment described p. 130). That baryta should take sulphuric acid from all other bases, although according to Berthollet's view its affinity for that acid must be the smallest, is explained by the great cohesion of sulphate of baryta: and that potash should separate lime and magnesia is supposed to result from the great cohesion of those earths, &c. It is certainly worthy of remark that when an acid is brought in contact with two salifiable bases, the least soluble body is always obtained: if one salt is less soluble than another, it is formed; if one base is less soluble than another, it is precipitated. Thus baryta takes sulphuric acid from strontia and forms with it an insoluble salt; strontia withdraws sulphuric acid from potash, and potash from soda,—sulphate of strontia being less soluble than sulphate of potash, and sulphate of potash than sulphate of soda. Soda takes lime from sulphuric acid, and the lime which separates is the least soluble body; lime takes sulphuric acid from magnesia, and magnesia is less soluble than lime. Ammonia alone forms an exception: it gives up sulphuric acid to lime, and the lime is thereby converted into the more soluble sulphate of lime. When a base comes in contact with

two acids, the same effect often takes place; sulphate of baryta is less soluble than nitrate, and this than hydrochlorate of baryta, &c. But on the other hand, the almost insoluble sulphite and carbonate of baryta are decomposed by nitric acid.

Bergman deduced from his analyses of various salts the two following laws which are directly opposed to Berthollet's theory: (1.) An acid has the greatest affinity for that base of which it takes up the greatest quantity. (2.) A base has likewise the greatest affinity for that acid of which the greatest quantity is required to neutralize the base.

Kirwan, from the results of his own analyses of salts, adopted the first of Bergman's laws; but with respect to the affinity of a base for different acids, he on the contrary laid down the law, that a base has the greatest affinity for that acid of which it takes up the smallest quantity.

All these laws could only have acquired an appearance of validity from the fact, that but a small number of acids and bases were examined in relation to them, and moreover in an inaccurate manner. Adopting the more exact quantitative relations at present known, and placing *all* the salifiable bases,—including those of the heavy metallic oxides—in the sulphuric acid column, and *all* the acids in the lime column, it will be plainly seen that decomposition by simple affinity has no fixed relation to proportional quantity. Moreover we now know that the latter depends on the atomic weight of bodies. If then the strength of affinity were determined by relative quantity, the former would bear a simple proportion, direct or inverse, to the atomic weight. Accordingly to Berthollet's law, the affinity of hydrogen for other bodies should be the greatest of all, since hydrogen has the smallest atomic weight, and therefore the smallest quantity of it suffices to saturate other bodies; the affinity of iodine on the contrary ought to be less than that of most other bodies, sulphur for example, since 126 parts of iodine are necessary to saturate a quantity of metal for which 16 parts of sulphur are sufficient; nevertheless iodine, though more volatile than sulphur, decomposes the metallic sulphurets.

General Laws, by which the Magnitude or Strength of Affinity is regulated.

1. *With regard to the same two bodies.* If A combines with different quantities of B, it holds the first quantity of B with greater force than the second, the second with greater force than the third, and so on. This law holds good without exception.

Carbonic acid, CO^2, in contact with hydrogen gas, zinc, iron, &c. at a red heat, gives up only 1 atom of oxygen, the other remaining—in consequence of the superior affinity of the carbon—united with it in the form of carbonic oxide, C O. Brown peroxide of lead, PbO^2, is reduced at a low red heat to red lead, Pb^3O^4, oxygen gas being evolved; the red lead at a stronger red heat gives up more oxygen and is converted into the yellow oxide, Pb O; and this will not part with its one atom of oxygen even at the most intense heat, but sublimes unchanged.

Apparent exceptions: Many combustible bodies abstract oxygen from nitrous oxide, N O, at a lower temperature than from nitric oxide, NO^2. This anomaly must be attributed to the hindrances which the gaseous state offers, in various degrees, to chemical action. The fact that nitric oxide is deprived of its second atom of oxygen by alkaline sulphites, and converted into nitrous oxide which suffers no further alteration from the

action of the same salts, proves the correctness of the law.—Nitric acid, $N O^5$, does not give up its oxygen to many bodies so easily as hyponitric acid, $N O^4$. But nitric acid, precisely on account of the small affinity of the nitrogen for the last atom of oxygen, is not known to exist in the separate state, but only in combination with water or salifiable bases. In aqueous nitric acid the great affinity of the water for the acid opposes, to a certain extent, the transfer of the oxygen to other bodies. So likewise hyperchlorate of potash, $K O, Cl O^7$, is less easily decomposed by heat and combustible bodies than chlorate of potash, $K O, Cl O^5$, although it contains two more atoms of oxygen. But hyperchloric acid is just on account of this greater quantity of oxygen a stronger acid than chloric acid, and the consequent greater affinity of potash for hyperchloric acid renders its decomposition more difficult.

2. *With regard to different bodies.* (*a.*) Simple substances exhibit the strongest affinities for each other, *e. g.* oxygen, chlorine, bromine, iodine, &c. towards most other elements. Then follow compounds of the first order, *e. g.* acids and salifiable bases. The affinities of compounds of the second order, salts, for instance, are much weaker. In proportion as the affinities of the elements are satisfied by combination, their tendency to form further combinations diminishes and ultimately ceases.

b. The more opposite bodies are in their physical properties, the greater for the most part is their affinity. Thus, metals being similar bodies have generally but little affinity for one another, but great affinity for oxygen, chlorine, bromine, iodine, sulphur, and other non-metallic bodies; in a similar manner, acids have little affinity for other acids or bases for other bases, but the affinity between acids and bases is very strong.

Columns of Affinity.

The following are a few columns of affinity drawn up principally from decompositions by simple affinity and from analogical reasoning. From the difficulty of the subject they must be considered as merely rough approximations. The bodies separated only by a comma are those whose relative position is as yet undecided; after each semicolon are placed substances whose affinity is decidedly weaker.

Oxygen: K; Na, Li; Ba, Sr, Ca; Mg, Ce, Y, G, Al, Th, Zr, Si; Ti, Ta, W, V, Cr, Mn; C O, H; Mo; Zn; Fe; Cd; Ni; Co; Sn; U; $Ta O^2$; Mn O; Mo O; Ti O; P; Pb; Bi; Sb; PO^3; S; Cu; $Mo O^2$; As; N; Sn O HCl; $S O^2$; $W O^2$; N O; Se; Pt Ir; Fe O S O^3; Hg; Te; Os; R; Pd; Ag; K O; Ba O; As O^3; I: NO^4; $Cr^2 O^3$, $V^2 O^3$; Au; Br; Cl; F; I O^5; Cl O^5; H O.

Chlorine: K and the other alkaline metals; metals which are the bases of the earths; Ti; Zn; Fe; Cd; Co; Sn; C O; H; P; Pb; Bi; Sb; S; Hg; As; Ag; Sn Cl; Hg^2 Cl; Pd; Pt; Au; I; Br; O.

Fluorine, Bromine, and *Iodine* are similar in their relations to chlorine.

Sulphur: O; K and the other alkaline metals; Zn, Fe; Sn; Cu; Cl; H; C; Pb; Bi; Sb; Hg; Ag; Pt; $Cu^2 S$; $Mo S^2$; Au.

Phosphorus: O; Cl; Br; I; K; Zn; S; H.

Hydrogen: O; F; Cl; Br; I; Se; S; P; As; Sb; N.

Nitrogen: C; H; I; Br; Cl.

Metals: O; F; Cl; Bs; I; Se; P; H. It is true that many metallic oxides and fluorides are decomposed at a red heat by chlorine; but in such cases the affinity of heat for the more vola[illegible]stances, oxygen and

fluorine, must be taken into account. Nevertheless the affinity of the noble metals for chlorine seems to be greater than for oxygen. On the whole it appears that different metals have different orders of affinity.

Sulphuric acid: Ba O; Sr O; K O; Na O; L O? Ca O; Mg O; Pb O; N H^3; Fe O; Zn O; Ni O; Co O; Cu O; $Al^2 O^3$; $Fe^2 O^3$. *Comp.* Shnaubert (*Unters. der Verwandtsch*, 57); Karsten (*Scher. 5, 583*); Gay-Lussac (*Ann. Chim.* 89, 21.)

Hydrochloric acid: 4Pb O; K O; Na O; Ba O; Sr O; Ca O; Mg O; N H^3; Co O; Ni O; Hg O; Ce O; Zn O; Mn O; Fe O; U O; Au O^3?; $Cu^2 O$; Cu O; Sn O; G O; $Al^2 O^3$; $U^2 O^3$; $Cr^2 O^3$; $Fe^2 O^3$; $Sn O^2$; $Bi^2 O^3$, $Sb O^3$. *Comp.* Schnaubert; Anfrye and Darcet (*A. Gehl*, 3, 325), Gay-Lussac, *a. a. O.*, and especially Persoz (*Ann. Chim. Phys.* 58, 180, also *J. Pr. Chem.* 6, 32). Persoz places the suboxide of copper above the protoxide, without however resting his supposition on experiment, and perhaps incorrectly. With regard to 4Pb O, *vid.* page 139.

Nitric Acid: K O; Na O; L O?; Ba O; Sr O; 6Pb O; Ca O; Mg O; N H^3; Ag O; Co O; Ni O; Ce O; Zn O; Mn O; Cd O; (6Pb O, N O^3); Cu O, G O; $Al^2 O^3$; $U^2 O^3$; $Cr^2 O^3$; $Hg^2 O$; Hg O; $Fe^2 O^3$; $Bi^2 O^3$; according to Schnaubert, Gay-Lussac, Anfrye and Darcet, and particularly according to Persoz. Here also the place assigned by Persoz to suboxide of mercury above the protoxide is to be doubted; according to Proust, (*A. Gehl*, I, 525) protoxide (red oxide) of mercury stands likewise above protoxide of copper, and according to Schnaubert, protoxide of manganese precedes protoxide of nickel.

For *phosphoric acid* the order appears to be as follows: Baryta, strontia, lime, potash, and soda; and for *oxalic acid:* Lime, baryta, strontia, magnesia, potash, soda, ammonia.

In the revision of these columns of acids particular attention should be paid to the formation of basic salts.

Potash: 2 At. Mo O^3; 2S O^3; 2Cr O^3; 2 At. oxalic acid: 2 At. tartaric acid; S O^3; Se O; N O^5; I O^7; Cl O^7; H F; H Cl; P O^5; As O^5; I O^5; Br O^5; Cl O^5; H Br; Cr O^3; P O^3; H I; Se O^2; N O^3; Mn O^7; Mn O^5; B O^3; C O^2; As O^3; H Se; H S; H Cy. This column is as yet very uncertain, and requires many corrections and additions.

Other bases exhibit orders of affinity more or less resembling that of potash.

VI. Origin and Nature of the Phenomena of Affinity.

1. *Atomic Hypothesis.*

According to the *Atomic* or *Corpuscular Theory*, matter is an original essence, and consists of certain very small parts called *Atoms, Molecules,* or *Particles,* arranged, not in absolute contact, but with *Intervals* or *Pores* between them; so that bodies, which to the eye appear perfectly continuous, like a piece of glass or metal, must be regarded, not as being completely filled with matter, but as aggregates of atoms and empty spaces. In chemical combination the heterogeneous atoms arrange themselves close to each other, but without penetration—*juxtaposition* takes place—and the aggregate of the so formed compound atoms, with the intervals or pores between them, constitutes the new compound. The ancient and modern atomic theories are distinguished from one another, according to the force which is supposed to act in bringing about the juxtaposition of the heterogeneous atoms.

A. Ancient Atomic Theory.

In this theory, the atoms are supposed to be actuated, not by any attractive force, but by a motion existing from all eternity—by virtue of which these atoms, invisible from their smallness, are continually falling through infinite space, but not in exactly parallel lines,—so that they sometimes come in contact and become aggregated together in larger masses, like the earth and the other bodies of the universe. Those atoms which go on moving alone, and so come in contact with bodies on the surface of the earth, sometimes fall without effect through their pores—sometimes, again, they strike on the atoms of the bodies, and thrust them either against the earth or against one another, thereby producing the phenomena of gravitation, cohesion, adhesion, and affinity. (Leucippus, Democritus, Epicurus, Lucretius, Lesage.)

B. Modern Atomic Theory.

According to this now almost universally preferred hyhothesis, the atoms are supposed to be imprest with innate forces which give rise to their mutual attraction, sometimes exhibited in the form of mechanical, sometimes in that of chemical force.

a. Constitution of Atoms.

Atoms are not infinitely small, in the mathematical sense of the words, but bodies of determinate magnitude, which cannot be separated into smaller parts, either by mechanical or other forces. They are of definite weight, definite magnitude, and definite form; and these are constant in the atoms of the same substance, but may differ in those of different substances. It is probable, however, that the atoms of all bodies have the same density, so that the weights of two heterogeneous atoms are in direct proportion to their volumes—and that if the atoms could place themselves side by side without leaving spaces between them, all bodies would have the same specific gravity, viz., that of the atoms. But there must exist between them considerable intervals, of various magnitudes in different substances,—and these are filled up with heat, the principle of elasticity,—whereby the atoms, which, by virtue of their mutual attraction, would place themselves in actual contact, are kept at certain distances from one another. When bodies are compressed or expanded, the atoms themselves suffer neither contraction nor expansion, but the pores are narrowed or widened. That atoms must be extremely small, and considerably less than $\frac{1}{6000000}$ line in diameter, is proved by the microscopal investigations of Ehrenberg. (*Pogg.* 24, 35.)

Respecting the *Form of Atoms*, two views are principally entertained.

According to one of these hypotheses, atoms have the same form as the fragments obtained by splitting a crystallized body in the direction of its planes of cleavage. Antimony, which may be cleft in directions parallel to the faces of an acute rhombohedron, is resolved by this mode of division into similar rhombohedrons of continually smaller and smaller dimensions; and if we conceive the cleavage to be carried to the utmost possible limit, the smallest rhombohedrons thus obtained will be the atoms of antimony. The atoms of a body which may be cleft parallel to the faces of a cube will have the form of a cube; [illegible] which may be cleft according to the faces of a six-sided prism [illegible] timately redu-

cible to triangular prisms. Cleavage according to the faces of a regular octohedron will give both regular octohedrons and tetrahedrons; hence one of these forms must belong to the atoms of a body so constituted, diamond for example. According to this view, atoms must have the form either of a parallelopiped (rhombohedron, cube, square, rectangular, or rhombic prism),—or of a triangular prism,—or of a tetrahedron or octohedron, regular or irregular. This theory certainly affords the easiest explanation of the crystalline form and determinate cleavage of simple substances; but it gives no explanation of amorphism—it does not accord well with dimorphism—and the more easily it explains the crystalline form of simple substances, the less is it adapted to account for that of compounds; for the juxtaposition of two or more atoms of different forms must produce a compound atom of very complicated figure.

Greater probability attaches, therefore, to the second theory, which has been particularly developed by Ampère (*Ann. Chim.* 90, 43). According to this theory, all atoms have a spherical form; and in the first place, these spherical atoms, by arranging themselves in various numbers and at various angles, produce aggregates possessing one or other of the forms which may be obtained by cleavage; these aggregates may be called crystalline molecules. Thus, 4 such spheres forming a base, and 4 placed perpendicularly over them, may produce a cube; so likewise may 3 layers of spheres, each containing 9, arranged in a square. Two or 4 such layers would give a flattened or elongated square prism; 2 or more rectangular layers of 6, 8, 12, or more spheres, placed one above the other, might produce a rectangular prism; 9 or 16 spheres arranged on a plane in the form of a rhombus, and 3 or 4 such layers one above another, would form a rhombohedron; 3 spheres below and 1 above, or 6 at the bottom, 3 above them, and 1 at the top, a tetrahedron; 3 spheres below and 3 above, a triangular prism, and so on. These crystalline molecules, formed at the earliest stage of crystallization, afterwards unite themselves, by attracting each other chiefly at their surfaces, into larger crystalline masses, separable in the directions according to which the junction has taken place—and thus planes of cleavage are determined. It is true that this theory leaves it at present unexplained, why the spheres should, according to the nature of the bodies to which they belong, unite themselves in different numbers and at different angles, whose magnitude is constant in each particular substance—and that thus sometimes one crystalline molecule, sometimes another, should be formed. But, on the other hand, it gives the best explanation of dimorphism and amorphism. When from viscosity in the liquid, or a too rapid passage from the fluid to the solid state, the atoms cannot first unite themselves in crystalline molecules in the manner just described, they all remain at equal distances from each other; consequently neither regular cleavage nor crystalline form can exist; that is to say, the body is in the amorphous state. Dimorphism arises when the atoms, according to temperature or other circumstances, unite themselves in different numbers and at different angles, into crystalline molecules of different forms, which, therefore, by their approximation, must produce crystals of different shape and cleavage. The compound atoms of compounds are aggregates of two or more spheres, and are capable of uniting to form crystalline molecules in the same manner as simple atoms.

With respect to ponderable fluids, it is supposed, according to the atomic theory, that each individual atom (whatever may be its form) is surrounded by a sphere of heat, which takes up but a small space in

liquids, but so large a space in gases that the volume of the atoms is utterly insignificant in comparison with that of the calorific envelopes. This greater and more uniform separation of the atoms by the calorific envelopes is supposed to account for the mobility of fluids. In different elastic fluids the calorific envelopes have different volumes: if the volume of the envelope surrounding an atom of sulphur = 1, the corresponding volumes in the other gases will be 3, 6, 9, 12, 18 or 24 (p. 55—67).

Of the correctness of the atomic theory, the following proof is adduced by Wollaston (*Ann. Phil.* 20, 251; *Gilb.* 72, 37). If matter were infinitely divisible, atmospheric air would by virtue of its elasticity expand into infinite space. The earth's atmosphere could not therefore have a definite limit, but must extend itself to the other heavenly bodies and form atmospheres around them, the density of which would be proportional to the mass and attractive power of these bodies. That no atmosphere is observed round the moon might perhaps be explained by the consideration that the lunar atmosphere, if it existed, must, on account of the small mass of the moon, be very rare and therefore imperceptible. But it may be astronomically demonstrated that the sun and Jupiter, whose masses are much larger than that of the earth, are likewise without atmospheres. Hence it follows that the air is not infinitely divisible, but that its atoms existing in the higher regions of the atmosphere do not separate from each other beyond that point at which their mutual repulsion is exactly balanced by their attraction towards the earth. Against this it may perhaps be alleged that even supposing the air to be infinitely divisible, its elasticity must at length be so much diminished by decrease of density that the earth's attraction will set bounds to the greater expansion which a further removal from the earth would involve. Moreover, if we admit, with Poisson and Dumas, that the uttermost parts of the air are, on account of the extreme cold there existing, in the solid or liquid state and surround the atmosphere in the form of snow-flakes of nitrogen and oxygen—the preceding demonstration will appear even less satisfactory.

b. Chemical Combination.

A chemical compound is produced, when one or more atoms of one substance arrange themselves in the most symmetrical manner possible by the side of one or more atoms of another substance, or of several other substances, and thus form a compound atom.—For the manner in which atoms arrange themselves one with another, *vid.* Gaudin (*Bibl. univ.* 52, 131).—Atoms are always more inclined to unite in simple than in complex numbers, and the more intimate compounds of the inorganic kingdom generally exhibit simple numerical proportions; while in organic compounds formed under the influence of the vital force, very complicated proportions are met with. Compound atoms again unite with compound atoms of a different kind to form compounds of the second order; and the compound atoms of the second order thus formed, by combining with others of the same order, give rise to compound atoms and combinations of the third order, and so on. The mode of conceiving the formation of the less intimate compounds of variable constitution, *e. g.* solutions of acids, alkalis or salts in arbitrary quantities of water—whether in such cases these bodies first form compound atoms of definite constitution by combining with a small quantity of water, and these are afterwards surrounded by the remaining atoms of the liquid, or whether the mixture takes place in some other way,—must for the present remain undecided.

A chemical combination therefore is a mixture continued as it were to the extreme of intimacy; in a mixture properly so called, whole masses of atoms of the one body are laid side by side with those of the other—and these heterogeneous masses can be distinguished by the senses. But in chemical combination the individual heterogeneous atoms are laid side by side; and since atoms—even compound ones—are too small to be individually discernible, the eye perceives only the masses formed by the heaping together of these atoms by virtue of cohesion, and hence the chemical compound appears homogeneous. These masses may indeed be separated into smaller and smaller ones by mechanical force, but their compound atoms are not thereby resolved into simple atoms; only the cohesion is overcome which holds together the compound atoms, not the affinity by which the simple atoms are united into compound ones.

With regard to the innate force by which atoms are disposed to combine, three hypotheses have been laid down. By some, it is regarded as the same universal force of attraction which under different circumstances exhibits itself as gravitation, cohesion, and adhesion; by others, as an attractive force of a peculiar nature; by others again as electricity.

First Hypothesis. Chemical combinations are produced by universal attraction.

Although Newton was the first who regarded chemical combination as the result of an attractive force, he nevertheless supposed that this force was different from universal attraction, and that it diminished according to the inverse cube of the distance. Buffon was the first to consider both these forces as identical. Since the force of universal attraction depends wholly on the mass of the attracting bodies and not at all upon their quality, while in chemical combination the latter is of the utmost importance, Buffon endeavoured to explain this difference by supposing that the centres of gravity of the atoms of heterogeneous substances might, in consequence of their difference of form, approach one another within different distances—and therefore, since the force of gravitation varies inversely as the square of the distance, the attraction between such bodies would vary in amount with the shape of their atoms.—Bergman also attributed these differences between the action of gravitation and that of affinity to the different forms of the atoms and likewise to their relative position.—Guyton-Morveau perceived that to explain the great difference in the strength of affinity depending on the nature of the bodies concerned, on the hypothesis of a difference of form in their atoms, was mathematically impossible: but he was nevertheless inclined—since, according to his view, strength of adhesion and strength of affinity follow the same laws—to regard affinity as a particular manifestation of the gravitation of the atoms, and to hope that the peculiar characteristics of affinity would be explained by the discovery of new facts.

Berthollet's Theory. Universal attraction is probably the cause of chemical combination. Its action in this respect exhibits peculiar characters, because it is exerted, not on masses, but on molecules placed at extremely small distances from each other, and differing in form, cohesion and elasticity. All bodies have affinity for all others: but the affinity is not always manifested, because other forces, such as gravitation, cohesion and elasticity overcome it (p. 35).

Two bodies are, by virtue of their affinity, essentially capable of uniting in all proportions; the exceptions to this law are to be attributed to the cohesion and elasticity, partly of the simple substances themselves, partly of the compound. Thus, water dissolves only a certain quantity of salt,

because the cohesion of the salt ultimately balances the affinity: similarly, the elasticity of a gas prevents its absorption by water beyond a certain limit, and the elasticity of oxygen gas causes metals to combine with only a definite quantity of oxygen. Moreover, if a combination in certain definite proportions, *e. g.* that of 76·6 baryta and 40 sulphuric acid possesses very great cohesion, it separates from the state of solution in water, becomes thereby removed from the sphere of chemical action, and consequently takes up no more of the excess of baryta or sulphuric acid which may perhaps exist in the liquid. For a similar reason, hydrogen and oxygen combine only in the proportion which forms the most coherent compound, viz. water; (the more coherent peroxide of hydrogen was not known at that time). This state of greatest cohesion corresponds, in most combinations of acids and bases, with the proportion which produces the most complete neutralization: but in compounds of the more coherent substances oxalic acid and tartaric acid with ammonia, potash, and soda, it is found in the acid salt.

The smaller the quantity which any substance requires of another to produce neutralization, the greater is their natural affinity (p. 142). Since, for example, according to the later more exact determinations, 47·2 parts of potash require 40 of sulphuric and 54 of nitric acid to neutralize them, the affinities of sulphuric and nitric acid for potash are to one another as 54 : 40. But in the chemical actions of bodies, not only their force of affinity, but also their quantity must be taken into account. If we assume, according to what precedes, that the affinity of a molecule of potash for a molecule of sulphuric acid amounts to 54, and for a molecule of nitric acid to 40, and suppose that 1 molecule of sulphuric acid and 3 molecules of nitric acid act simultaneously on 1 molecule of potash,—the force with which the sulphuric acid tends to lay hold of the potash will be $1 . 54$, and that exerted by the nitric acid $3 . 40 = 120$. This product of the force of affinity into the quantity of the acting substance is called by Berthollet the *Chemical Mass*. Hence the chemical force of a body increases in direct proportion to its quantity; and a substance possessing but small affinity may, when its quantity is in excess, exert a stronger attraction on a third body than other substances possessing intrinsically greater affinity but present in smaller quantity.

When a body A comes in contact with two bodies B and C, both of which tend to combine with A, it does not combine exclusively with that one for which it has the greater affinity, not even when the quantity of the latter is sufficient for the complete saturation of A; neither does it combine exclusively with the one which acts with the greater chemical mass, but divides itself between the two in the proportion of their chemical masses. If, according to the preceding example, 1 molecule of sulphuric acid and 3 of nitric acid act on 1 of potash, the chemical mass of the sulphuric acid being $1 . 54$ and that of the nitric acid $3 . 40 = 120$, $\frac{54}{174}$ of the quantity of potash present combines with the sulphuric acid, and $\frac{120}{174}$ with the nitric.

This law—that a body divides itself between two others which are endeavouring to lay hold of it, in the proportion of their chemical masses—is subject to exceptions, only when in such conflicts of affinity, a change in the state of aggregation of one of the acting bodies or one of the compounds, is produced by cohesion or elasticity, and these bodies are thus removed from the sphere of chemical action. In such cases A may combine exclusively with B or C. Hence arise the four following cases.

1. The cohesion of B effects its complete separation; *e. g.* When ammonia is added to an aqueous solution of sulphate of alumina, the sulphuric acid at first divides itself between the two bases in the ratio of their chemical masses; but since the alumina is thus deprived of a portion of its sulphuric acid, and the remainder is not sufficient to hold all the alumina in solution, a portion of it is precipitated and thus removed from the sphere of chemical action: now since by this precipitation, the quantity of alumina contained in the solution, and therefore also its chemical mass, is diminished, the ammonia is enabled to rob it of another portion of sulphuric acid, thereby precipitating more alumina, diminishing the chemical mass of that which remains dissolved, again removing sulphuric acid, and so on,—till at length it appropriates all the acid and throws down the whole of the alumina. These successive decompositions follow each other so quickly, that the whole action seems to take place in a moment.

2. The elasticity of B effects its complete separation; *e. g.* When hydrochloric acid is added to a solution of carbonate of potash in water, the potash at first divides itself between the two acids: the compound thus formed of part of the potash with the whole of the carbonic acid allows however a part of the carbonic acid, now less intimately combined, to escape as gas and thus to remove itself from the sphere of action; the chemical mass of the carbonic acid in the solution being thus diminished, the hydrochloric acid takes from it a fresh portion of potash, and sets free another portion of carbonic acid—and thus the action is repeated, as in the former case, till the whole of the potash has combined with the hydrochloric acid, and the whole of the carbonic acid has escaped.

3. The cohesion of A C effects the complete separation of B; *e. g.* If baryta dissolved in water be brought in contact with a mixture of sulphuric and nitric acids, in such proportion that for every molecule of baryta present there shall be 1 molecule of sulphuric and 3 of nitric acid, the baryta will at the commencement be divided between the two acids in the same proportion as the potash in the example above given. But potash forms with both the acids soluble salts, which therefore remain mixed; whereas the compound of baryta with a certain quantity of sulphuric acid is insoluble, falls down, and is removed from the sphere of action. The solution now contains, besides the combination of baryta with nitric acid, the excess of sulphuric acid which the precipitated sulphate of baryta was unable to take up. This free sulphuric acid takes from the nitric acid, in proportion to its chemical mass, a new quantity of baryta, which however is precipitated in combination with the proportional quantity of sulphuric acid; this sets free another portion of sulphuric acid, which again takes baryta from the nitric acid; and this repeated abstraction and precipitation goes on till all the baryta is thrown down in the form of sulphate and all the nitric acid is set free. In accordance with this explanation, Berthollet supposes that on bringing together two salts, whose acids as well as bases are different, four salts are always produced: thus nitrate of potash and sulphate of soda in solution produce a mixture which still contains a portion of these salts in the undecomposed state, together with sulphate of potash and nitrate of soda. In general therefore four salts are obtained; but if one of the two new salts is insoluble and separates itself from the sphere of action, the undecomposed salts yet remaining in solution produce, in consequence of the equal division of their elements, a new quantity of the insoluble salt; but as this always falls down, the decomposition goes on till the two original

salts are completely decomposed;—*e. g.*, nitrate of baryta and sulphate of soda.

4. The elasticity of A C effects the complete separation of B; *e. g.* When peroxide of iron is heated to redness with charcoal, the oxygen ought to divide itself between the iron and the carbon in proportion to their chemical masses. But since the oxygen which combines with the carbon forms carbonic oxide, which escapes as gas and so becomes removed from the sphere of action, the remaining carbon continues to withdraw oxygen from the iron, till the latter is completely reduced to the metallic state.

Review of Berthollet's Theory.—1. This theory does not establish the identity between affinity and universal attraction. Berthollet himself supposes that different bodies have very different degrees of affinity for one another, without specifying to what extent the individual qualities of the molecules may exert a peculiar influence on their mutual gravitation and thus modify the laws of universal attraction.

2. Unacquainted with our present system of stoïchiometry, Berthollet supposed that two bodies can combine in any proportions whatever, and endeavoured to explain the fact that combination generally takes place in a few definite proportions only, by assuming that precisely when these proportions hold good, the compound possesses the greatest density, cohesion, or elasticity. But why does chlorine gas combine with hydrogen gas in one proportion only, and then without any condensation or expansion produce hydrochloric acid gas?

3. It is true that the quantity of a substance exerts some influence on its manifestations of affinity (p. 125); but unless adhesion also comes into play, this influence is not exerted by any quantity beyond that which is still capable of entering into combination. For example, since one atom of oxygen cannot combine with more than one atom of carbon, 100 atoms of carbon will have no more effect on the combination of any substance with one atom of oxygen than a single atom of carbon would; if this one atom cannot abstract the oxygen, neither will 100 atoms do it.

4. Berthollet's theory—that a body A divides itself between the bodies B and C in the proportion of their chemical masses—has an appearance of truth in those cases only in which the substances which act upon each other are contained in a liquid in which both they and their possible compounds are soluble; because in such cases it cannot for the most part be directly shown what compounds are contained in the liquid, whether A C and B according to the ordinary view, or A B and A C according to Berthollet's. But in some cases even of this kind, the incorrectness of Berthollet's theory may be distinctly shown. Boracic acid colours litmus wine-red, sulphuric acid turns it bright red. Now if sulphuric acid be gradually added to a warm solution of borate of soda in water which has been coloured blue with litmus, the liquid at first remains blue, because a combination of soda with excess of boracic acid is produced; on the addition of more sulphuric acid, boracic acid is set free, and colours the liquid wine-red; and not till all the soda has entered into combination with the sulphuric acid does a further addition of that acid give the liquid a bright red colour; but if sulphuric acid were present at the commencement of the action, either in the free state or combined with sulphate of soda in the form of an acid salt, the bright red colour would appear at once. (Gay-Lussac, *Ann. Chim. Phys.* 49, 323; also *Pogg.* 25, 619.) From the same cause, a solution of sulphate of potash or soda to which boracic acid has been added colours litmus only wine-red; but the

addition of $\frac{1}{3000}$ of sulphuric acid immediately produces the bright red tint. (Dubail. *J. Pharm.* 18, 425). Hence boracic acid does not take soda from sulphuric acid or set that acid free. Hydrosulphuric acid and carbonic acid exhibit similar relations towards sulphuric acid. (Dumas.)—Tincture of litmus is instantly bleached by chlorine water, but not till after several days by aqueous solution of iodine: now, a solution of chloride of sodium mixed with iodine should, according to Berthollet, produce a mixture containing chloride of sodium with excess of chlorine, and iodide of sodium with excess of iodine. But the orange-yellow mixture colours litmus green (from the yellow of the solution and the blue of the tincture): and a very small quantity of chlorine water immediately changes this green colour into the orange-yellow of the solution of iodine: this shows that no chlorine had been set free by the iodine. (Dubail; Gm.)—Phosphate of peroxide of iron is soluble in hydrochloric acid, but not in acetic acid. From its solution in hydrochloric acid it is completely precipitated by acetate of potash. Now if the potash had been divided between the hydrochloric and acetic acids, part of the hydrochloric acid would have remained free, and would have held some of the phosphate of iron in solution. (Gay-Lussac *a. a. O;* also *Ann. Chim. Phys.* 70, 416.—Compare also Persoz. *Chim. molecul.* 346.)—The experiments of Soubeiran and O. Henry (*J. Pharm.* 11, 430, also *Mag. Pharm.* 15, 44, also *N. Tr.* 12, 1, 266) do not prove much in favour of Berthollet's views.

Other objections to Berthollet's theory of distribution may be deduced from the following facts. Oxalate of lead digested with water and as much sulphuric acid as is necessary to saturate the oxide of lead, is completely resolved into sulphate of lead and free oxalic acid. (Pfaff. *Ann. Chim.* 77, 266): Berthollet's remarks on this experiment (*Ann. Chim.* 77, 288,) are not satisfactory.—Hyperiodate of lead digested with water and a quantity of sulphuric acid somewhat less than that required to take up all the oxide of lead, yields a solution of hyperiodic acid free from sulphuric acid and from hyperiodate of lead. (Benckiser. *Ann. Pharm.* 17, 257.)—Chloride of silver mixed with water is easily converted by iron into metallic silver and chloride of iron, the latter remaining in solution. According to Berthollet the contrary result should be produced, since iron is more coherent than silver, and chloride of silver is insoluble in water, while chloride of iron is soluble. These last experiments likewise show that insoluble substances, such as oxalate of lead, chloride of silver, &c., are by no means removed from the sphere of chemical action.—Similarly Gay-Lussac has shown (*Ann. Chim.* 89, 21) that a metallic oxide insoluble in water may completely precipitate another from its solution in acids (*e. g.*, oxide of zinc may precipitate oxide of silver), provided it be added in sufficient quantity to saturate the acid.—3 atoms of iron fused with one atom of tersulphuret of antimony completely separate the antimony from the sulphur, though no solid or gaseous compound is formed, the melted sulphuret of iron lying in a stratum above the melted antimony.

It has also been shown (page 130) that hydrochloric acid decomposes carbonate of lime, and forms with the lime a perfectly neutral solution, even under a pressure sufficient to liquefy carbonic acid. Now since the hydrochlorate of lime is soluble and the carbonate insoluble, the contrary effect ought to be produced, according to Berthollet, as soon as the escape of carbonic acid is prevented. In a similar manner, hydrochloric acid decomposes sulphite of lime, although that salt is nearly insoluble, and sulphurous acid has less elasticity than hydrochloric acid, inasmuch as it is liquefied by smaller pressure.

To Berthollet must be conceded the great merit of having closely scrutinized the theory of affinity, examined it in a new light, and directed attention to the influence exerted by cohesion and elasticity on the manifestations of affinity. But he laid too little stress on the magnitude of affinity, and too much on the quantity in which substances act, and on the influence of cohesion and elasticity. He erroneously supposed that a body which separates in the solid state is removed from the sphere of action, that bodies are capable of combining in all proportions, and that a substance divides itself between two others in the proportion of their chemical masses.

Second Hypothesis. Chemical combinations are produced by a peculiar power, called Affinity, different from universal attraction.

So long as it is assumed that universal attraction, as manifested in gravitation, acts only in proportion to the mass, and that the peculiar nature of a substance has no influence on its amount,—it is difficult to refer the manifestations of cohesion and adhesion, and impossible to attribute those of affinity, to its action. In chemical phenomena, the quality of a substance above all things determines the existence and strength of the attraction, and its influence cannot be replaced by that of quantity. Moreover, a high degree of affinity must be ascribed to the imponderable bodies, which are not subject to the laws of gravitation. So long therefore as it shall remain undemonstrated that gravitation is influenced by quality of matter, and that the hitherto so-called Imponderables possess weight,—or else that the phenomena hitherto attributed to the affinities of these bodies are really due to other causes—so long will it be most advisable (as indeed most chemists at least tacitly do) to regard affinity as a peculiar power distinct from all others.

Third Hypothesis. The union of heterogeneous atoms is the result of Electrical Attraction. (*Electrochemical Theories*).

In some of these theories a common fundamental power is assumed which shows itself, sometimes as electrical, sometimes as chemical force; in others the combinations of ponderable substances, uninfluenced by any affinity of their own, are supposed to arise merely from the mutual attraction of the two electricities attached to their atoms, which attraction is itself regarded as a kind of affinity.

To the list of electro-chemical theories belong those of Winterl (*N. Gehl.* 6, 1 and 201);—of Sir H. Davy (*N. Gehl.* 5, 41, also *Elem. of the Chemical Part of Nat. Phil.*);—of Dumas (*Phil. of Chem.* p. 369), further developed and contested by Grotthuss (*Phys. Chem. Investigations*, 1, 44);—of Ampère (*Pogg.* 2, 185);—of Becquerel (*Ann. Chim. Phys.* 24, 192);—of Ferré (*Ann. Chim. Phys.* 28, 417);—of Schweigger (*Schw.* 5, 49; 6, 250; 7, 302 and 515; 8, 307; 11, 54, 330 and 435; 14, 510; 25, 158; 39, 214; 40, 9; 44, 79; 52, 67);—and of Fechner (*Schw.* 52, 27).

The electro-chemical theory of Berzelius demands, as the fullest and most consecutive, a more detailed explanation.—Compounds usually called chemical are divided into two classes. The *less intimate* whose formation is attended with lowering of temperature—*e. g.* solutions of salts in water—must be regarded (since all solid bodies are not soluble in water) as resulting from a specific attraction (comp. page 34 1, 2); the atoms of the solid body diffuse themselves through the liquid, till each atom is surrounded by an equal number of atoms of the liquid.—The *more intimate* compounds are the really chemical or electro-chemical combinations. These result, not from any mutual affinity between their ponderable elements, but from that of the electricities attached to their atoms. The atom of each substance has two poles, on which the two opposite electricities

are accumulated in different proportions, according to the nature of the bodies. The atom of many bodies, oxygen for instance, has a large quantity of negative electricity attached to one of its poles, and but a very small quantity of positive electricity at the other; that of other bodies, potassium for example, has a large quantity of positive electricity at one pole and very little negative electricity at the other. Thus the elementary substances are divided into *electro-negative* and *electro-positive*. To each element however there belongs a particular proportion between the quantities of the two electricities. Oxygen has, of all the electro-negative elements, the greatest quantity of negative electricity at one of its poles and the smallest quantity of positive electricity at the other—then follows sulphur, then nitrogen, &c., and lastly hydrogen, in which the quantities of the two electricities are nearly equal. Of all electro-positive substances, potassium has the largest quantity of positive and the smallest of negative electricity; and this inequality continually diminishes in other bodies, till we come to gold, in which the positive electricity predominates but little over the negative—so that this element occupies the next place to hydrogen. According to this, the elements succeed one another in the electro-chemical series of Berzelius as follows, beginning with the electro-negative.

Electro-negative: O, S, N, F, Cl, Br, I, Se, P, As, Cr, V, Mo, W, B, C, Sb, Te, Ta, Ti, Si, H.

Electro-positive: Au, Os, Ir, Pt, Rh, Pd, Hg, Ag, Cu, U, Bi, Sn, Pb, Cd, Co, Ni, Fe, Zn, Mn, Ce, Th, Zr, Al, Y, G, Mg, Ca, Sr, Ba, L, Na, K.

In the combination of an electro-negative with an electro-positive body, the predominant negative electricity of the former unites with the predominant positive electricity of the latter. Before, however, combination takes place, the former substance exhibits negative, and the latter positive electricity in the free state; and the tension of the two electricities continually increases as the bodies approach the temperature at which combination takes place. Hence we have an explanation of *electricity by contact*. At the instant of combination, the negative poles of the atoms of the first body turn themselves towards the positive poles of those of the second; and since it is only in the fluid state that the atoms possess the mobility necessary for this arrangement, it follows that solid bodies have, generally speaking, no chemical action on one another. The two electricities of these poles now combine and produce heat or fire, whereupon they disappear. In every chemical combination, therefore, a neutralization of the opposite electricities takes place, by which heat or fire is produced in the same manner as in the discharge of the electrical pile or of lightning, excepting that these last-mentioned phenomena are not accompanied by any chemical combination, at least of ponderable bodies. Every chemical combination is therefore an electrical phenomenon depending on the electrical polarity of the atoms.

Since the electrical series does not accord with the order of affinity—since for example, the highly electro-negative substance oxygen has, according to experiment, less tendency to combine with the electro-positive body gold than with sulphur which stands next to oxygen in the electrical series—Berzelius supposes that, although in the atom of gold the positive electricity of the one pole is of greater amount than the negative electrity of the other, nevertheless the absolute quantity of positive electricity existing at one pole of the atom of gold is less than that which is present at one pole of the atom of sulphur,—the latter containing however a much greater quantity of negative electricity at its other pole than the

gold-atom possesses. Suppose for instance that the quantity of negative electricity at one pole of the gold-atom = 1, of the positive electricity at the other = 2, of the negative at one pole of the sulphur-atom = 12, and that of the positive at the other pole = 4; then the positive electricity will predominate in the gold-atom and the negative in the sulphur, but the sulphur will possess a much higher degree of *electrical polarization* than the gold; the positive electricity accumulated at its positive pole will therefore be able to neutralize a greater quantity of negative electricity in the oxygen than the positive electricity of the gold; hence the greater tendency of oxygen to combine with sulphur than with gold.

In the same body, the degree of electrical polarisation,—*i. e.* the absolute quantity of the two electricities in the atomic poles—varies, according to Berzelius, with the temperature, and is generally increased by elevation of temperature. Many bodies, such as carbon, which appear to have but very weak polarisation at common temperatures, often become highly polarized at a red heat,—hence their combination with oxygen at that temperature. Many substances, on the contrary, such as gold, which have altogether but weak polarization, frequently show it in a greater degree at low than at high temperatures, at which indeed it often disappears entirely.

Electro-negative bodies in combination with oxygen generally form electro-negative compounds; *e. g.* sulphur produces sulphuric acid; electro-positive substances give electro-positive compounds; *e. g.* potassium produces potash.

The decomposition of a compound produced by electro-chemical neutralization can only take place when the elements have their former polarity restored to them. That the united elements, after the neutralization of their opposite electrical states, are held together by a force which resists all mechanical means of separation, does not result from any innate power (affinity); otherwise the permanence of the combination would not be subject to the influence of electricity. But the most intimate chemical combination may be destroyed by restoring the electrical polarity of the elements. In this decomposition of compounds by the electrical current, the acting electricities disappear and the elements reassume their former chemical and electrical properties. If A B is resolved by C into A C and B, C must have greater intensity of electrical polarization than B. Hence there results more complete neutralization between A and C than that which before existed between A and B; this gives rise to development of heat, and B reappears with its original polarity. A substance capable of combining with others, sometimes as an electro-positive sometimes as an electro-negative element, can only be separated from the first mentioned combinations by bodies still more positive, and from the latter by bodies still more negative: *e. g.* sulphur can only be separated from its combinations with oxygen by bodies which are more positive, and from its combination with lead by bodies which are more negative than itself.

This theory of Berzelius is encumbered with the following difficulties:—(1). No precise demarcation can be drawn between the less intimate chemical combinations supposed to be produced by affinity and the more intimate ones which are ascribed to electrical action. At all events it does not seem conformable to nature to assume the existence of two totally different causes for these two very similar classes of compounds. According to this view, one atom of sulphuric acid should combine with the first two or three atoms of water, not by affinity but by electrical attraction,

and with any further quantity of water by affinity. Now if sulphuric acid combined with three atoms of water, possess affinity for water, why should not the same acid when pure or when combined with one atom of water, also have affinity for water?—(2). What is it that induces the two electricities to accumulate each by itself in definite quantity, on two opposite points of an atom which must be regarded as a homogeneous mass? What prevents their combination? Are the atoms of all bodies, even of metals, perfect non-conductors? Again, when sulphur and lead are melted together, the negative electricity of the sulphur-atoms is supposed by Berzelius to combine with the positive electricity of the lead-atoms, the combination being accompanied by a development of light and heat. Why does not the negative electricity at one pole of an atom of sulphur combine with the positive electricity at the opposite pole of another atom and produce fire, when the sulphur is melted by itself?—(3). If combinations are produced not by the affinity of the elements but by electrical polarity, every substance, simple or compound, should be capable of combining with every other whose atomic poles contain the two electricities in different proportions; why, for example, should the predominating positive electricity of mercury combine with the negative electricity of tellurium and not with that of carbon?—(4). It is not easy to discover by what force combined substances are held together. The heterogeneous atoms unite in consequence of their adhesion to the opposite electricities; but when these have been neutralized by combination, it might be expected that the atoms would fall asunder and allow themselves to be easily separated by friction and other mechanical forces, which is by no means the case. In order to overcome this difficulty, Dumas supposes (*Philos. of Chem.*) that in the combination of oxygen and hydrogen, for example, the negative pole of the former places itself towards the positive pole of the latter, and the positive pole of the former towards the negative pole of the latter; moreover, that the atoms can only give up the electricity of one of their poles—that it is only on this side that electrical neutralization takes place, viz., of the negative electricity of the oxygen with the positive of the hydrogen—that on the contrary the electricities of the two other poles, viz., the positive of the oxygen and the negative of the hydrogen remain uncombined, and hold the atoms united by their mutual attraction. But this assumption—that the electricity of only one pole of an atom can combine with the opposite electricity of another, and that those of the other poles are incapable of uniting—would not only be a new enigma, but admits of positive contradiction; for in the combination of sulphur with oxygen, the *positive* electricity of the sulphur must unite with the negative of the oxygen; and in the combination of sulphur with the metals, its *negative* electricity with the positive of the metal. Einbrodt's explanation (*Ann. Chim. Phys.* 61, 262; also *J. pr. Chem.* 8, 345,) agrees in the main with that of Dumas.

The theory adopted in the present work is as follows:—Ponderable bodies have affinity for one another. The two electricities are substances which likewise possess affinity for each other, and by whose combination in the proportions in which they neutralize each other, heat (fire) is produced. The individual electricities, and likewise heat, have considerable affinity for ponderable substances, and are united to them with greater force and in greater quantity, the more simple these ponderable substances are. Ponderable bodies, according to their nature, have a greater or less excess of positive or negative electricity united with them in addition to a definite quantity of heat. Thus, oxygen probably contains the greatest

quantity of positive, and potassium of *negative* electricity. Bodies lying between these two extremes contain a larger quantity of heat with a smaller excess of one or the other kind of electricity, the proportion of which varies greatly according to their nature,—and thus form an electrical series which perhaps coincides with the column of affinity of oxygen (p. 144).

The combination of two ponderable bodies is the result of two forces, viz., the affinity of the ponderable bodies for each other, and the affinity of the electricity which is in excess in the one body for the opposite electricity which predominates in the other. By these two forces the affinity of the electro-negative body for the positive electricity united with it, and that of the electro-positive body for the negative electricity combined with it, are overcome. The result is heat and the ponderable compound. The latter retains the excess of positive or negative electricity, by which it acquires either an electro-negative or electro-positive character, and likewise part of the heat—while another portion is set free, and gives rise to the development of heat or fire, by which most chemical combinations are accompanied. When combination takes place between two bodies, both of which contain an excess of the same kind of electricity—*e. g.*, oxygen and sulphur, which contain free positive electricity in different quantities,—it is simplest to suppose that the combination is the result merely of the affinity between the two ponderable bodies, that the new compound contains the sum of the excesses of positive electricity, and that the development of heat is a consequence of the inability of the new compound to retain as much heat united with it as was before combined with its constituents.

When a ponderable compound is decomposed by elevation of temperature—*e. g.* oxide of silver at a red heat into oxygen gas and silver—it may be supposed that the affinity of silver for negative electricity + that of oxygen for positive electricity + that of heat for oxygen is greater than the affinity of silver for oxygen + that of the two electricities for each other. Hence part of the heat is resolved into its elements and unites as negative electricity with the silver and positive with the oxygen (*Sch.* 101). The decompositions of ponderable compounds by ponderable substances may perhaps take place as follows. When chlorine at a red heat expels oxygen from potash, forming chloride of potassium, it transfers that portion of positive electricity, which in combining with pure potassium it would have given up to the negative electricity of that substance —to the oxygen which has lost its own positive electricity by combining with the potassium (*Sch.* 102).—When potassium in contact with water produces potash and hydrogen gas, the negative electricity of the potassium goes over to the disengaged hydrogen, which in forming water had previously given up its own negative electricity to the positive electricity of the oxygen (*Sch.* 103). The same takes place in the solution of zinc in dilute sulphuric acid: its negative electricity goes over to the escaping hydrogen gas (*Sch.* 104). [For the explanation of the decomposition of compounds by the electric current according to this hypothesis, vid. *Electricity.*]

2. *Dynamic Hypothesis.*

A substance which to our senses appears continuous, like glass, is likewise so in reality: it does not therefore consist of atoms and empty spaces, but fills completely the space included between its surfaces. Matter is therefore capable of expanding and contracting by virtue of its

own intrinsic nature, not in consequence of the widening or narrowing of pores contained within it. In chemical combination, the elements have the power of diffusing themselves through each other without limit, so that in the smallest point of the compound both elements are alike present;—the elements do not lay themselves side by side—they *penetrate each other.*

A. Kant's Theory.

Matter is a self-existent essence, and is actuated by two forces, the force of attraction and the force of repulsion. It may indeed be pressed together by external force, but only to a certain point,—for its repulsive force increases with the condensation. The action of different kinds of matter on each other, whereby through their innate forces they alter the combination of each other's parts, is chemical action; it consists sometimes in solution, sometimes in decomposition. A perfect solution would be such as, in its smallest particles, would contain the heterogeneous substances in the same proportion as in the whole. Kant however leaves it undecided whether such a solution is ever actually formed; but it may be imagined—for if the action of the solvent power be continued, the division must still go on and that without limit, so that ultimately the volume of the solution will be uniformly filled with each of the two elements at the same time, and thus they will have penetrated each other. (Kant, *Anfangsgr. d. Naturwissenschaft.* Aufl. 3, s. 75.)

B. Schelling's Theory.

Matter is not an original essence, but derives its origin from the conflict of the attractive and the repulsive force; and its various qualities depend upon the quantitative relation of these primary forces. Chemical action takes place only between heterogeneous bodies, those namely, in one of which the relation between the primary forces is the reverse of that in the other. The resulting compound is the mean dynamical ratio of the primary forces which have been brought into activity during the process, and consequently its properties differ essentially from those of its elements. (Schelling, *Ideen zu einer Philosophie der Natur.* Aufl. 2, 1803, s. 453.)

[Faraday: *Speculation concerning the Nature of Matter. Phil. Mag. J.* 24, 136.]

PART II.

SPECIAL CHEMISTRY,

OR

THEORY OF THE AFFINITY OF INDIVIDUAL SUBSTANCES.

SECTION I.

Chemistry of Imponderable Bodies.

The Imponderable Bodies, Imponderables, Ethereal Substances, Radiant Powers, or Incoercibles, are distinguished from ponderable substances chiefly by the following characters.

1. They are without weight, so far at least as our balances can show.

2. They are in the highest degree expansible,—and therefore when unequally distributed diffuse themselves—for the most part quickly and by radiation in straight lines—through those spaces which offer no opposition to their progress.

3. They penetrate bodies which are impenetrable to all ponderable substances.

4. Generally speaking, they manifest themselves directly to but few of our senses; magnetism to none, light and heat to one, only electricity alone to several.

The properties here noticed certainly render it doubtful whether the sensations of light, heat, &c., should be attributed to the direct action of peculiar kinds of matter, or whether they are not rather caused by the vibrations of certain supposed elastic fluids of extreme tenuity, like the luminous ether, &c.; the former supposition is however the simpler of the two, and better adapted than the latter to a chemical view of the subject.—According to the undulatory theory, the coloured rays of light are distinguished from one another by the different breadths of the waves of the luminous ether; and when they all fall on the eye together, they produce the sensation of pure colourless light. How different would be the impression produced by the whole series of sound-waves if they were all to invade the ear at once!

The Imponderables are: Light, Heat, Electricity and Magnetism:—As these substances are all fully discussed in physics, we shall in this work confine ourselves principally to the chemical relations of the first three towards ponderable bodies,—omitting magnetism, which appears to exert no influence on the chemical relations of ponderable bodies.

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SYNONYMES. *Luminous Substance, Light-producing Matter, Luminous Matter, Lumière, Photogène.*

Light is that substance which excites in our eyes the sensation of brightness or vision.

Physical Properties.

1. Light is imponderable.
2. It is in the highest degree expansible: it spreads itself out from its

point of origin in straight lines or *Rays* with extraordinary quickness, passing over 42,100 miles in a second. Its intensity varies inversely as the square of the distance from the luminous source.

3. It penetrates the air and all other *transparent* bodies more or less completely; whilst *opaque* bodies either do not transmit it at all, or only when they are in very thin laminæ.

4. When in passing through a transparent medium it falls on other bodies, transparent or opaque, it is partly *thrown* back or *reflected*,—and in such a manner that the incident and reflected rays make equal angles with the reflecting surface.

5. When a ray of light travelling through a thin medium passes near a denser body, its course is somewhat altered,—it is *inflected*—it suffers a *bending* or *Inflexion*.

6. When a ray of light passes in an oblique direction from one medium to another of different density and combustibility, its course is likewise altered; the light is *broken* or *Refracted*. If the second medium is denser or more combustible than the first, the ray is bent towards the perpendicular,—and conversely.

Inflexion and refraction may perhaps be explained by supposing the attraction or adhesion of bodies for light to increase with their density and combustibility.

7. *Dispersion of Colour.*—At every refraction, a colourless ray of light is separated into seven coloured rays. These are, beginning with the most refrangible: violet, indigo, blue, green, yellow, orange, red. [*Luminous* and *Coloured Spectra.*] The yellow and green rays are the most luminous. Far beyond the boundary of the violet there exists, according to Seebeck, a faint violet light which gradually becomes colourless*: similarly, red light exists beyond the assigned limit of the red. None of the coloured rays experience any further change of colour by a second refraction.

8. When light falls at a particular angle (35° for glass) on the surface of a body, the reflected light is found to possess peculiar properties; it is *Polarized*. For, if the ray thus reflected fall on a second flat surface of the same body at the same angle, it is completely reflected therefrom, when the second surface is parallel to the first or makes a right angle with it; but no reflection takes place when the second surface is turned round through an angle of 90°, so that the ray which falls on the first surface would make a right angle with the ray reflected from the second†.

9. In a great number of media, viz., in crystals not belonging to the regular system, and in certain uncrystallized animal substances, a ray of light is split into two distinct rays oppositely polarized: *Double Refraction. Comp.* Brewster (*Edinburgh J. of Sc.* 5, 1; also *Schw.* 33, 340).

* The existence of luminous rays having a faint violet or rather a *lavender grey* colour has likewise been proved by Sir John Herschel (*Phil. Trans.* 1840, Pt. I.)

† The ray is completely reflected when the planes of incidence on the first and second surfaces coincide: no reflection takes place when they are perpendicular to each other. [W.]

CHEMICAL RELATIONS OF LIGHT.

1. Relations of Light to the other Imponderables.

1. *Relation of Light to Heat.*

A. Development of Heat by Light.

All ponderable bodies absorb a portion of the light with which they come in contact. The quantity thus absorbed is greater in proportion to their opacity, and the darkness and roughness of their surfaces. Transparent bodies, with white shining surfaces, absorb the least, inasmuch as the greater part of the light which falls on them is either transmitted or reflected. The more light a body absorbs, the hotter does it become when exposed to the sun's rays.

In sunshine which raises a mercurial thermometer to 38° C. (100° Fah.) a ball of pure bismuth, one inch in diameter, rises to 50°; the same ball, covered with indian ink, to 56°; with lamp-black, to 59°; and with white paint to 43°: when covered with a blue colour, the ball is more strongly heated than when clean; but less strongly when painted red. (Böckmann.)—If a number of pieces of copper of equal sizes are covered with various colours, the black becomes most heated in the sun, then the blue, then the red and green, then the yellow, and lastly the white. (H. Davy.)—Pieces of cloth laid upon snow in the sunshine sink deeper the darker they are in colour. (Franklin.)

[*Heat-collector* of Saussure and Ducarchat.]

The concentration of the sun's rays by means of burning glasses or mirrors is one of the most powerful means of producing a high temperature.

Flaugergues has shown, by experiments made during a solar eclipse, that the light of the sun has the same heating power, whether it proceeds from the edge of the disc or from the centre.

Daniell's supposition, that the solar rays have less heat-producing power at the equator than in the temperate regions, has been shown by Gay-Lussac (*Ann. Chim. Phys.* 26, 375) and Foggo (*Edinb. Phil. J.* 14, 63) to be incorrect.

The light of the sun loses but very little of its heating power by passing through a plate of glass.

Solar light refracted through a prism shows the greatest heating power: according to Landriani, in the yellow; according to Rochon, between the yellow and the red; according to Herschel and Englefield, beyond the utmost limit of the red; according to Bérard, at the furthest edge of the red, whilst the heating power of the almost invisible rays situated beyond the red is only $\frac{1}{2}$ as great; according to Leslie, in the red, whilst beyond the red scarcely any heating effect was produced. Seebeck however has shown that the heating power of the coloured rays varies with the nature of the prism. According to that philosopher, the heating power of the coloured rays gradually increases from the extreme edge of the violet or about $\frac{1}{2}$ an inch beyond it (where it is weakest) through the blue and green, and attains its maximum:—with a prism filled with water, in the yellow; with a prism filled with oil of vitriol, or with a solution of sal-ammoniac and corrosive sublimate together, between the yellow and the red; with a prism of common white glass and crown glass, in the full red; and with a prism of flint-glass, beyond the red.

Whatever may be the nature of the prism, heat is always manifested beyond the red, but gradually diminishes as the distance from the extreme limit of the red increases. With a prism of rock-salt the maximum of heat is situated far beyond the red. The solar light contains heating rays of various degrees of refrangibility; rock-salt transmits them all, even the least refrangible; glass and water only the more refrangible: for this reason the maximum of heat, when prisms of glass or water are used, is found within the coloured spectrum. (Melloni.) According to Powell, the heating power of the coloured rays depends also upon the colour of the body to be heated; according to his observations, a thermometer painted with vermilion is more strongly heated in the orange rays than in the red. According to the same philosopher, the heating rays of the prism pass like the solar rays through glass without perceptible loss of heating power.—There exists therefore a *Heat-spectrum* in connection with the coloured spectrum. According to Herschel, the coloured spectrum takes up only about $\frac{3}{5}$ of the space occupied by the heat-spectrum; and in consequence of the smaller refrangibility of the heat-rays, the focus of heat is somewhat farther (according to Wollaston about $\frac{1}{12}$) from the burning glass than the focus of light.

¶ Sir John Herschel (*Phil. Mag. J.* 22, 505) has obtained some remarkable results by exposing thin writing paper, blackened on one side by holding it over a smoky flame, and afterwards thoroughly wetted with alcohol applied to the unsmoked side, to the action of the solar spectrum. The influence of the calorific rays was shown by a whitening of the paper, marking by a clear and sharp outline the lateral extent of these rays, and by due gradations of intensity in a longitudinal direction, their law or scale of distribution, both within and without the luminous spectrum. The thermic spectrum thus impressed extended from about the middle of the violet to a distance considerably beyond the red; moreover, it was found to consist of a number of distinct patches, the brightest of which were situated in and just beyond the visible red rays. Three other spots subsequently came into view at continually greater distances from the luminous spectrum and successively diminishing in brightness. This want of continuity in the thermic spectrum may arise from an absorbent effect in the atmosphere of the sun, or of the earth, or of both; if such absorbent action be exerted by the earth's atmosphere, it will follow that a large portion of the solar heat never reaches the earth's surface at all, and that the heat incident on the summits of lofty mountains differs, not only in quantity but also in *quality*, from that which the plains receive. ¶

The two spectra formed by a prism of double refracting spar have equal heating powers. (Bérard.)

Moonlight, the intensity of which, according to Bouguer, is to that of sunlight as 1 : from 250000 to 30000, produces, when concentrated by a burning mirror, only a very slight degree of heat barely perceptible by a delicate thermometer (Howard, *Sillim. Amer. J.* 2, 327); according to most observers is has no effect on the thermometer; and Forbes (*Phil. Mag. J.* 6, 138) observed no trace of heating, when he caused moonlight concentrated 3000 times by a glass lens to fall on a thermo-multiplier.

B. *Development of Light by Heat.*

All bodies when heated to a certain temperature become incandescent. Iron becomes hot when hammered; by long-continued hammering it

may be made red-hot.—All bodies become red-hot at the same temperature,—excepting that air requires, according to Wedgewood's experiments, a higher temperature to render it luminous. According to Newton, iron becomes dull red in the dark at 335° C. (635° Fah.), bright red at 400° C. (752° Fah.), luminous in the twilight at 474° C. (903° Fah.), and luminous in bright daylight at about 538° C. (1000° Fah.)

Modes of explaining the facts stated in A and B.

1. Light and heat are the same substance. Light arrested in its motion by the adhesion of ponderable bodies shows itself as heat. When too much heat becomes accumulated in a body, part of it escapes again with great velocity in the form of light: the body becomes incandescent.

Against this very simple theory—to which Berthollet also (*Stat. Chim.* 1, 191) gives the preference—the following objections may be urged: (*a*). Moonlight, ever so much concentrated gives no heat. (This may perhaps be explained by its very small intensity.)—(*b*). The brightest, most luminous rays of the coloured spectrum, the yellow and green, give very little heat, and the heating power likewise shows itself where neither light nor colour can be perceived.—Light produces chemical alterations of ponderable bodies, which heat alone is unable to effect. (This may perhaps be explained by the more rapid motion of light.)—Phosphorescence by Irradiation, and more particularly that produced by heating, is difficult to reconcile with this hypothesis.

2. The solar rays consist of rays of light and rays of heat distinct from one another; the former are more refrangible than the latter; hence two spectra of different kinds. The solar rays give heat therefore only in consequence of the heat which they contain. The solar light reflected to the earth from the moon has left its heat-rays on the moon and therefore cannot give heat. (Herschel.)

Objections: (*a*). What becomes of the rays of light which bodies absorb together with the rays of heat, seeing that the bodies suffer no change from the absorption, excepting change of temperature?—(*b*). Why cannot a body become very hot without emitting light?

3. All ponderable substances contain the hypothetical *Principle of Fire*, which, when united with the light which falls on them, produces heat. (Deluc.)

2. *Relation of Light to Electricity.*

Light often appears as an attendant of electrical phenomena:—the electrical spark, lightning. Is it an element of electricity, or on the other hand is light composed of the two electricities—or is it merely separated by electricity from the surrounding medium?

3. *Relation of Light to Magnetism.*

If the violet ray of the spectrum concentrated by a lens be made to pass uniformly for about half an hour over one half of a steel needle, proceeding from the middle towards one of the extremities, that extremity being directed to the north, and the temperature being between 0° and 27° C. the needle will become perfectly magnetic. (Morichini, *Schw.* 20, 16; further in *Kastn. Arch.* 8, 105.—This experiment was also successfully made by Ridolfi (*Schw.* 20, 10), Mary Somerville (*Ann. Phil.* 27, 224; abstr. *Pogg.* 6, 493), Müller (*Kastn. Archiv.* 13, 397), Baumgartner (*Zeitschr. Ph. Math.* 1, 263), Zantedeschi (*Bibl. univ.* 41, 64; also *Schw.* 56, 109; also *Pogg.* 16, 187), and Barlocci (*Bibl. univ.* 42, 11; also *Schw.* 58, 69). It did not succeed in the hands of Configliachi (*Gilb.* 46, 335),

Ries & Moser (*Pogg.* 16, 563) and d'Hombres Firmas (*Ann. Chim. Phys.* 10, 285).—I have myself seen it successfully performed by Morichini.

¶ All former researches on the relation between light and magnetism have been completely thrown into the shade by the important discovery of Faraday (*Phil. Trans.* 1846, I, 1)—that a ray of polarized light, when made to pass through certain transparent substances placed near a magnetic pole, in such a manner that the *lines of magnetic force** shall pass through it in the direction of the ray,—is rotated in a particular direction, depending upon the direction of the ray itself and that of the line of magnetic force. —I shall give, nearly in Dr. Faraday's own words, the description of the experiment which first revealed this most remarkable phenomenon.

A ray of light issuing from an Argand lamp was polarized in a horizontal plane by reflection from a surface of glass, and the polarized ray passed through a Nichol's eye-piece revolving on a horizontal axis, so as to be easily examined by the latter. Between the polarizing mirror and the eye-piece, two powerful electro-magnetic poles were arranged, being either the poles of a horse-shoe magnet, or the contrary poles of two cylinder magnets; they were separated from each other about two inches in the direction of the ray, and so placed that, if on the same side of the polarized ray, it might pass near them; or if on the contrary sides, it might go between them, its direction being always parallel or nearly so to the magnetic lines of force. After that, any transparent substance placed between the two poles would have passing through it, both the polarized ray and the magnetic lines of force, at the same time and in the same direction.

A piece of *heavy glass* consisting of silico-borate of lead (*Phil. Trans.* 1830, p. 1) about two inches square and half an inch thick, having flat and polished edges, was placed as a *diamagnetic*† between the poles (not as yet magnetized by the electric current) so that the polarized ray might pass through its length. The glass acted as air, water, or any other indifferent substance would do; and if the eye-piece were previously turned into such a position that the polarized ray was extinguished, or rather the image produced by it rendered invisible, then the introduction of the glass made no alteration in this respect. In this state of circumstances, the force of the electro-magnet was developed by sending an electric current through its coils, and immediately the lamp-flame became visible, and continued so as long as the arrangement continued magnetic. On stopping the electric current, and so causing the magnetic force to cease, the light instantly disappeared. These phenomena could be renewed at pleasure at any instant of time, and upon any occasion, showing a perfect dependence of cause and effect.

The voltaic current was that of five pair of Grove's construction, and the electro-magnets were of such power that the poles would singly sustain a weight of from 28 to 56lbs or more.

By various experiments made in this manner, it was found that the character of the force thus impressed upon the diamagnetic is that of *rotation*, and that it acts according to the following law:

"If a magnetic line of force be *going from* a north pole or *coming from*

* The term *Line of magnetic force* or *Magnetic line of force*, or *Magnetic curve*, denotes that exercise of magnetic force which is exerted in the lines usually called *magnetic curves*, and which equally exist as passing from or to magnetic poles or forming concentric circles round an electric current.

† A *diamagnetic* is a body through which lines of magnetic force are passing, and which does not by their action assume the usual magnetic condition of iron or loadstone.

a south pole along the path of a polarized ray coming to the observer, it will rotate that ray to the right-hand; or if such a line of force be coming from a north pole or going from a south pole, it will rotate such a ray to the *left hand.*"

It was likewise found that the degree of rotation is proportional to the extent of the diamagnetic through which the ray and the lines of magnetic force pass. The power of rotating the ray of light increases with the intensity of the magnetic lines of force.

Other bodies besides the *heavy glass* possess the power of acting on light under the influence of the magnetic force. When those bodies have a rotative power of their own—as is the case with oil of turpentine, sugar, &c.—the effect of the magnetic force is to add to or subtract from their specific force, according as the natural rotation and that induced by the magnetic force are in the same or in opposite directions.

The silico-borate of lead was found to be the best substance for exhibiting the phenomena. Fused borate of lead is nearly as good: flint-glass exhibits the rotation, but in a less degree, and crown-glass still less. Crystallized bodies exhibit little or no influence on the ray when under magnetic influence. All liquids which have been submitted to experiment produce the rotation: air and the other gaseous bodies do not. The following table gives an approximate estimate of the relative amount of the induced rotating force in a few substances, as compared with the natural rotating force of a specimen of oil of turpentine. (Water = 1.)

Oil of turpentine	11·8
Heavy glass	6·0
Flint-glass	2·8
Rock-salt	2·2
Water	1·0
Alcohol	less than water
Ether	less than alcohol.

The rotating force is also induced by ordinary magnets in the same manner as by electro-magnets, but in a less degree, simply because the magnetic force exerted by the former is less than that exerted by the latter.

By placing various transparent bodies within long helices of wire through which powerful electric currents were passing—it was found that "When an electric current passes round a ray of polarized light in a "direction perpendicular to the ray, it causes the ray to revolve on its "axis, as long as it is under the influence of the current, in the *same* "*direction* as that in which the current is passing." It will be easily seen that this law is *identical* with that previously stated respecting the rotating power induced by the magnet.

In all cases it is found that the interposition of copper, lead, silver, and other ordinary non-magnetic bodies in the course of the magnetic curves, either between the poles and the diamagnetic, or in other positions, produces no effect on the phenomena, either in kind or in degree. Iron affects the results in a remarkable degree; but it always appears to act either by altering the direction of the magnetic lines or by disposing of their force within itself.

No rotating power is induced by lines of *electro-static tension.*

The results here described, important as they are in themselves, become still more so when viewed in connection with the magnetic condition of all matter, as developed in the 20th and 21st series of Faraday's *Experimental Researches.* A brief abstract of these researches will be found at the end of Chap. III.

II. Relations of Light towards Ponderable Bodies.

1. *Changes produced in Ponderable Bodies by the Action of Light.*

Chemical effects of Light.

A. Combinations produced by the agency of Light.

a. Chlorine gas does not combine with hydrogen to form hydrochloric acid gas at ordinary temperatures and in the dark, but only under the influence of light (Gay-Lussac & Thénard): according to Seebeck, the combination takes place under white or blue, but not under red glass. Neither does sunlight transmitted through bichromate of potash effect the combination. (Draper: vid. *Formation of Hydrochloric Acid.*)—*b.* Chlorine gas combines with carbonic oxide gas only under the influence of light. (J. Davy.)—*c.* Iodine and olefiant gas combine only in sunshine. (Faraday.)—*d.* Many kinds of plate-glass, which have only a faint violet tint, become purple after exposure to light for a year, while the same glass kept in the dark retains its original pale tint. (Faraday, *Qu. J. of Sc.* 15, 164; also *Pogg.* 24, 387.) This may arise from a higher oxidation of the manganese contained in the glass.—*e.* Hyacinths exposed to light lose their reddish tint and become browner. (G. F. Richter, *Pogg.* 24, 386.) This case belongs perhaps to the head of decompositions.

B. Combinations accompanied by Decompositions.

a. Phosphorus kept in various gases or in water, is changed in the sunshine under colourless or blue glass (not however, or but very slowly, under red) into red oxide of phosphorus. (Böckmann, A. Vogel.) Hence light brings about the combination of the phosphorus with the oxygen of the air or of the water.—*b.* Chlorine combines at ordinary temperatures with the hydrogen of water and liberates oxygen gas, but only under the influence of light.—Aqueous solution of chloride of platinum mixed with lime water gives a precipitate in colourless or violet, but not in red or yellow light. (Herschel.)—*d.* Chlorine decomposes light carburetted hydrogen gas when moist, forming hydrochloric acid and carbonic acid, but only when exposed to light. (W. Henry.)—*e.* Chlorine converts the oil of olefiant gas at under temperatures into chloride of carbon and hydrochloric acid, but only under the influence of light. (Faraday.)—*f.* The oil of olefiant gas covered with water and placed in the sunshine is resolved into hydrochloric acid and acetic ether. (Mitscherlich.)—Chlorine converts anhydrous hydrocyanic acid under the influence of the sun's rays into hydrochloric acid and solid chloride of cyanogen; it also decomposes moist cyanide of mercury in different ways accordingly as light is concerned in the action or not. (Serullas.)—*h.* The brown solution of iodine in absolute alcohol saturated with sulphurous acid gas deposits crystalline sulphur when exposed to sunshine. (Döbereiner, *Pneumat. Chem.* 5, 72.)

i. Many metallic oxides combined with acids and dissolved in alcohol or ether give up oxygen, only under the influence of light, to these organic liquids, and are thus either brought to a lower degree of oxidation or reduced to the metallic state. Yellow hydrochlorate of peroxide of uranium dissolved in ether is converted by light into precipitated dark

hydrochlorate of protoxide of uranium. (Gehlen.)—Hydrochlorate of peroxide of iron dissolved in ether is resolved under white and blue, not under red glass, into hydrochlorate of protoxide of iron. (A. Vogel.)—Red sulph-hydrocyanate of peroxide of iron is converted into colourless sulph-hydrocyanate of protoxide of iron (in the focus of a concave mirror in a few minutes,—more quickly by the bluish green ray of the spectrum than by any other—and even by the light of an Argand lamp placed at the distance of an inch. (Grotthuss.)—Hydrochlorate of protoxide of copper dissolved in alcohol or ether is reduced to dichloride of copper. (Gehlen, Neumann, *Schw.* 13, 358.)—Hydrochlorate of protoxide of mercury (corrosive sublimate) is converted under white or blue, but not under red glass, into calomel. (A. Vogel.)—Hydrochlorate of oxide of gold dissolved in ether or alcohol is discoloured on exposure to light, and according to Grotthuss, most quickly in the blue ray, metallic gold being separated;—also hydrochlorate of oxide of platinum dissolved in ether deposits a small quantity of platinum when exposed to light, and is at the same time considerably decolorized. (Gehlen.)—*k.* The red aqueous solution of oxalate of sesqui-oxide of manganese loses its colour when exposed to sunshine (slowly in blue and violet light) and is converted into carbonic acid and oxalate of protoxide of manganese. (Döbereiner.)—Aqueous oxalate of peroxide of iron is resolved, when exposed to the direct rays of the sun, into carbonic acid and oxalate of protoxide of iron. The change also takes place in violet and blue, but not in yellow or red light, neither is it produced by boiling. (Döbereiner.)—Oxalic acid added to aqueous solutions of hydrochlorate of oxide of gold, hydrochlorate of oxide of platinum, and ammonio-chloride of iridium, precipitates the metal and generates carbonic acid. In the case of iridium, the action cannot be replaced by that of a boiling heat. (Döbereiner, *Schw.* 62, 90.)—An aqueous solution of tartrate of peroxide of iron and potash, containing copper, deposits metallic copper on the side exposed to light. (Ehrmann, *Repert.* 49, 112.)—*l.* Many other organic substances also take oxygen from metallic oxides dissolved in acids, only when their action is assisted by light. Thus, charcoal and oils precipitate the pure metals from gold and silver solutions only when exposed to light or at a boiling heat. (Rumford.) Linen marked with nitrate of oxide of silver blackens only when exposed to light. Paper moistened with solution of gold reddens in presence of light,—and likewise in the dark, when it has been exposed to light till the reddening has commenced. (Seebeck.)

m. Light favours the combination of the oxygen of the atmosphere with the carbon and hydrogen of organic substances, by which they are more or less decomposed and altered. In this manner may be explained the decolorization and rotting of fabrics coloured with safflower, logwood, Brazil wood, turmeric, and woad when exposed to the sun—an effect which, according to Gay-Lussac & Thénard, is likewise produced in the dark by heating them to 160°...200° C. with access of air [Chevreul's investigations on the behaviour of tissues or fabrics dyed with various colouring matters and placed in different media: vid. *Ann. Chim. Phys.* 66, 71];—the decoloration of the petals of *Papaver Rheas*, which according to A. Vogel takes place more quickly through blue than through white glass;—the blanching of the blue flowers of *Cichorium sylvestre*, which takes place more rapidly in fine than in dull weather (Pajot Descharmes, *J. Phys.* 95, 112);—the decoloration of the green tincture obtained by digesting the green leaves of plants in alcohol (this tincture, according to Grotthuss retains its colour longest in the blue-green ray of the spectrum);—the

decoloration of the yellow oils of linseed, savin, and peppermint, and the yellow colouring of blue oil of camomile and colourless oil of turpentine.—In a similar manner may also be explained the green colouring of yellow guiacum—either pulverized or spread upon paper by means of an alcoholic solution—when exposed either to colourless or violet light in a glass containing air or oxygen gas, or when strongly heated, whereas concentrated red light restores the yellow colour. (Wollaston, *Gilb.* 39, 291.) [See also Herschel, *Phil. Mag. J.* 22, 5.]

n. The blue solution of iodide of starch in water is completely decolorized, with development of hydriodic acid, by colourless light and by the yellow and green ray of the spectrum (in the focus of a concave mirror the effect takes place in a few minutes),—slightly by the red and blue, and not at all by the violet, the last on the contrary counteracting the decolorizing action of daylight. (Grotthuss.)

o. The green parts of living plants, under the influence of light decompose carbonic acid, liberating oxygen gas from it and retaining the carbon, which enters into organic combinations. In this case also the violet appears to be the most active of the coloured rays, whilst under yellow glass plants become paler. (Senebier, Tessier.) Moonlight and candle-light appear also, according to Tessier and Vasalli, to have some effect.

C. Decompositions produced by Light.

a. Salts containing water of crystallization lose it when exposed to the sun, and much more quickly behind blue than behind red glass. (A. Vogel.)

b. Concentrated nitric acid is decomposed by exposure to light (as also by a red heat) into oxygen gas and hyponitric acid, NO^4 (Scheele); and according to Seebeck, this effect is produced behind white and blue, but not behind orange-coloured glass.

c. Many metallic oxides, when exposed to light, give up the whole or a part of their oxygen, and are resolved into pure metal and a higher oxide. Thus, brown peroxide of lead is resolved into oxygen gas and red lead (the latter becomes of a darker colour by the long continued action of light: the cause of this phenomenon remains to be discovered);—grey oxide of mercury is resolved into metallic mercury and red oxide;—the red oxide, under water, is decomposed, according to Seebeck, into mercury, grey oxide, and oxygen gas, provided that the light comes to it through colourless or blue glass, not through red;—(dry red oxide of mercury loses in four months under colourless glass 0·9, under violet 0·5, under green 0·2 and under red 0·1 per cent. of oxygen acquiring at the same time a grey colour, which is strongest under colourless, and scarcely observable under red glass. *Dulk.*)—Oxide of silver is resolved into silver and oxygen gas;—carbonate of silver into silver, oxygen and carbonic acid gas;—(pyrophosphate of silver blackens on exposure to the light);—oxide of gold into gold and oxygen gas. (Scheele.)—Manganic acid dissolved in water and exposed to sunshine slowly deposits peroxide of manganese, while oxygen gas is set free. (Fromherz.)

d. Proto-chloride of mercury dissolved in water is resolved in sunshine into dichloride of mercury, hydrochloric acid, and oxygen gas. (Boullay.)—Terchloride of gold dissolved in water deposits flakes of gold when exposed to the sun. (Scheele.)

e. White chloride of silver, as obtained by precipitating nitrate of silver with hydrochloric acid or a soluble chloride, changes when exposed

to the direct rays of the sun or to ordinary daylight, first to violet and then to black, giving up at the same time a portion of its chlorine.—According to Vasalli, this change of colour takes place in moonlight concentrated by a powerful lens,—but according to Gay-Lussac it does not. (*Ann. Chim. Phys.* 19, 215.)—The chloride of silver becomes coloured in the light diffused by a cylinder of lime on which the flame of a spirit-lamp fed by a stream of oxygen gas is directed. (Drummond, *Ed. J. of Sc.* 9, 319; *Pogg.* 9, 172; also *Schw.* 48, 434.)—It likewise blackens in the light of the twyer of a cast iron furnace fed with coke. (Mallet, *Phil. Mag. J.* 14, 475.)—It does not become coloured in the very bright light produced by the combustion of olefiant gas. (Brande, *Ann. Chim. Phys.* 19, 205.)

Chloride of silver precipitated in a finely divided state upon paper is peculiarly sensitive to the action of light.

Daguerre's Chloride of Silver Paper.—Thin or unsized paper is saturated, either by immersion or by means of a painting brush, with hydrochloric ether which has become somewhat acid by long standing; it is then dried at the ordinary temperature of the air or a little above it, dipped in a solution of nitrate of silver—or else the solution is merely applied to the surface—and dried in the dark at a very gentle heat (because while yet damp, it is not blackened by the calorific rays of non-luminous bodies) and kept closely pressed in a portfolio to preserve it from light and air. This paper when exposed to day-light blackens very quickly: its sensibility is diminished by age. According to the kind of paper used and the liquid—whether hydrochloric ether or some other liquid containing chlorine—with which it has been wetted, the colours produced by the light exhibit different tones. This paper blackens slowly and faintly in the light of a Locatelli's lamp with two wicks: still more faintly from the rays of iron heated below redness, provided these rays have not passed through a glass-plate; not by the rays from a vessel filled with boiling water, nor by repeated electric discharges. (Biot.)

Talbot's Chloride of Silver Paper.—Good writing paper is steeped in solution of common salt, wiped dry in order to spread the salt uniformly over it, washed on one side with solution of nitrate of silver, and dried by the fire. The paper loses its sensibility in a few weeks, but regains it on being again washed with nitrate of silver, and in a still higher degree by being alternately dipped in solution of common salt, moistened with nitrate of silver, and dried. When a light-picture has been produced on this paper, it is immediately washed with solution of common salt or iodide of potassium, to prevent the rest of the paper from blackening.

Paper dipped in solution of chloride of barium and afterwards in nitrate of silver is very susceptible, and becomes coloured in five minutes in a strong gas-light flame. (Hunt.)

If the light from a clouded sky be allowed to fall on Daguerre's paper, either directly or through plates of different colourless bodies, it is found that the blackening is least diminished when the plate consists of gypsum (Fraueneis); then follows rock-crystal, then white, then colourless glass, and lastly, animal gelatine. (*Glas-papier.*)

When sunlight falls on chloride of silver paper after passing through glass cisterns containing various colourless liquids, the blackening is accelerated if the cistern contains water instead of air, but with other fluids it is either retarded or unaltered. If the retarding influence of air be assumed = 1, that of water = 0·7645; of hydrochloric acid of sp. gr.

1·1907, it is equal to 1·2344; of nitric acid of 1·355 sp. gr. it is 1·4872; of sulphuret of carbon 1·4964; of oil of copaiba 1·7044; of oil of turpentine 1·7644; of hydrobenzoyl 2·0034; of oil of lemons 2·8258; of oil of rosemary 3·0172; of oil of lavender 3·1405; and of creosote 3·9597. No action is exerted by glacial acetic acid, wood-spirit, acetate of methyl, benzoate of methyl, absolute alcohol, ether, oxalic ether, acetic ether, acetone, oil of olefiant gas, or chloride of benzoyl. (Malaguti.)

Of all substances hitherto examined, the following give the freest passage to the chemical rays: Air and other colourless gases, aqueous vapour, water, alcohol, and ether.—Then follow: (2). Oil of vitrol, nitric acid, nitre, carbonate of soda, double refracting spar, English plate-glass, aqueous hydrocyanic acid, and camphor.—(3). The vapours of iodine and hyponitric acid—alum, red fluor-spar, crown-glass, flint-glass, French and German plate-glass, mica, and gum-arabic.—(4). Other kinds of plate, flint, and crown-glass, green fluor-spar, creosote, oils of anise, caraway, peppermint, lavender, rosemary, savine, and violet, Canada balsam and amber.—(5). Least pervious to the chemical rays are green bottle-glass, chlorine gas, oxide of chlorine gas, vapour of bromine, liquid bromine, and glass slightly smoked. (Hunt.)

Of all the rays of the spectrum the violet has the greatest blackening power. (Scheele, *Von der Luft und dem Feuer*, 72.) When paper covered with chloride of silver is exposed to the luminous spectrum, it becomes reddish brown beyond and in the violet rays, blue or bluish grey in the blue, very slightly yellow or not at all coloured in the yellow, reddish in the red, faintly reddish beyond the red;—moreover, with flint-glass prisms, which give the maximum of heating power beyond the red ray, the reddening of the chloride of silver also takes place beyond the red. (Seebeck.) Chloride of silver which has become grey from exposure to daylight, turns paler and reddish after a time in the red ray; in the red produced by the union of the violet of one spectrum with the red of another, the chloride of silver becomes of a beautiful crimson red. (Seebeck.)—The part of the spectrum from the red to the green, concentrated by a lens, gives a dazzling focus which does not blacken chloride of silver even in two hours. (Bérard.)

The spectrum likewise exhibits chemical effects beyond the violet ray, as was discovered by Ritter and established by Wollaston. According to Bérard, the extreme edge of the violet shows the strongest chemical action. The following experiments however show that the point of greatest action varies with the nature of the prism.

When the rays of the sun are made to fall by means of a heliostat through prisms of different kinds, on paper which has been moistened with gum-water and then sprinkled with powdered chloride of silver, the blackening takes place with different degrees of quickness and extends over different spaces, according to the nature of the prism: the maximum effect is also produced at different parts of the spectrum.

Bb. denotes bright blue, Bl. blue, V. violet, E. edge of the violet, D. dark space beyond the violet, Bd. border.

A. Material of the prism.—B. Time at which the blackening begins.—C. Intensity of blackening.—D. Extent *in lines* of the blackening.—E. Boundaries of the blackening.—F. Point of greatest blackening.

A.	B.	C.	D.	E.	F.
			Lin.	from to	
Alcohol	immediately			Bb — 4 Lin. in D.	V. ½ from Bl.
Oil of turpentine	13 minutes			3 Lin. in Bl. — 1½ — in D.	V. ⅓ from Bl.
Water	¼ „	very strong	13	2 — in Bl. — 1⅔ — in D.	V. middle
Oil of almonds..	2⅔ „	very weak	12	Bd. of Bl. — 2 — in D.	V. middle
Solution of blue vitriol	½ „	very strong	12½	1½ Lin. in Bl. — 1 — in D.	V. ⅓ from R.
Ordinary bluish glass	½ „	moderate	19½	2 — in Bl. — 2 — in D.	V. near to R.
Sol. of acetate of lead	3 „		14	Bd. of Bl. — 4 — in D.	R.
Oil of anise	1 „	weak	36	Bd. of Bl. — far in D.	R.
Crown-glass....	1½ „		18	Bd. of Bl. — 4 Lin. in D.	R.
Flint-glass	2½ „	weak	42	V. middle — 31 — in D.	in D. 3 Lin. from R.
Oil of cassia ..	12 „	very weak	84	Bd. of yellow — 36 — in D.	in D. 23 Lin. from R.

From this it appears that the position of the maximum of blackening depends neither on the density of the refracting medium nor on its refractive or dispersive power. (Hessler.)

Chloride of silver blackens under violet, blue, and bluish green glasses: under yellowish green and yellow glasses it remains almost unchanged, under orange-coloured glass it acquires only a faint red tint after a considerable time: chloride of silver blackened by light soon becomes lighter and of a dirty yellow or red colour when placed under orange-coloured glass. (Seebeck.)

Chloride of silver paper does not become coloured in sunlight which has passed through the following yellow liquids, even when it is concentrated by a lens: solution of neutral chromate of potash, of quinto-sulphuret of ammonium, of quinto-sulphuret of calcium, of sesqui-chloride of iron, of terchloride of gold, or bichloride of platinum, also yellow vegetable infusions. Under a solution of bichromate of potash it becomes in five days of a pale yellow green; under a solution of red ferrocyanide of potassium it becomes of a tile-red, and under ammoniuret of copper of a greenish brown tint. (Draper, *Phil. Mag. J.* 16, 81.)

According to the nature of the chloride used to saturate the paper, which is afterwards dipped in silver solution, the chloride of silver acquires various colours under different coloured glasses:

	Under blue	green	yellow	red glass:
Sal-ammoniac	olive brown	pale brown	brown	deep orange
Chloride of potassium	bright purple	sky blue	bright violet	red
Chloride of sodium ..	purple	blue	violet	red-brown
Chloride of barium ..	purple	black	red-brown	pale red
Chloride of calcium ..	rich violet	pale blue	blue	reddish
Chloride of manganese	rich brown	reddish	pale rose	yellow
Proto-chlor. iron	red	colourless	pale red	leaden
Sesqui-chlor. iron	blue	yellowish	straw-coloured	yellow green

Paper prepared with chloride of barium is coloured yellow by light which passes through chlorine gas, and red by that which passes through vapour of hyponitric acid. Light passing through bromine vapour does not colour paper prepared with sal-ammoniac. (Hunt.)

been allowed to remain on it for half a minute, it must be dried lightly with blotting paper. This operation requires the total exclusion of daylight. The paper prepared in this manner is exquisitely sensitive, exposure of less than a second to diffused daylight being quite sufficient to produce a decided effect upon it.

The calotype paper may be used for taking portraits from the life by means of the camera obscura. It is the only paper yet discovered sufficiently sensitive for this purpose. When properly prepared, it yields pictures of exquisite beauty and fidelity. It likewise serves for taking representations of buildings, scenery, &c. The picture, as first produced, is generally latent and invisible, but may be brought out immediately by again washing the paper with a mixture of 1 part of the silver solution with 3 parts of the saturated solution of gallic acid. In cold weather, the development of the picture may be accelerated by holding it over a basin of hot water.—The picture being thus obtained, it is to be fixed by washing in clean water, lightly drying between blotting paper, and then washing it over with a solution of bromide of potassium, containing 100 gr. of that salt in 8 or 10 ounces of water: after a minute or two, it is to be again well washed with water and then finally dried. Where bromide of potassium is not at hand, a strong solution of common salt may be used in its stead.

The calotype picture is a negative one,—but positive copies may be obtained from it by placing it with its face against the sensitive side of a piece of ordinary photographic paper (Talbot's chloride of silver paper already described), pressing it into close contact by a board below and a glass above, and exposing it for a short time to good sunshine.—A more sensitive copying paper may be prepared by soaking letter paper for a minute in a solution of salt and water—one oz. of salt to a gallon of water—drying it, and then washing it over with a mixture made by adding to a solution of 70 grains of nitrate of silver in an ounce of water sufficient caustic ammonia to nearly redissolve the precipitate at first produced.—The positive pictures are fixed by washing in water and immersion for ten minutes in a solution of hyposulphite of soda (1 oz. to a pint of water)—then finally washing and drying.

Since the calotype was first patented, some further improvements have been made by Mr. Talbot, among which may be mentioned: 1. The removal of the yellowish tint of the iodide of silver from the paper, by immersing the picture for about ten minutes in a bath consisting of a solution of hyposulphite of soda in ten times its weight of water and heated nearly to the boiling point,—then well washing and drying it. [A stronger solution of the hyposulphite may also be used cold, the paper being immersed in it for a longer time: this will be found the more convenient method of the two.] After this, the picture is placed upon a hot iron and wax melted into its pores to increase its transparency. The excess of wax is removed by pressing between blotting paper with a hot iron.—2. Rendering the calotype paper more sensitive by placing a warm iron behind it in the camera while the light is acting upon it.—3. The improvement of photographic drawings by exposing them twice the usual time to the action of sunlight. The shadows are thus rendered too dark and the lights are not sufficiently white. The drawing is then washed, and plunged into a bath of iodide of potassium of the strength of 500 grains to a pint of water, and allowed to remain in it for a minute or two, which makes the picture brighter and causes its lights to assume a pale yellow tint. It is then washed, and immersed in a hot bath of hyposul-

phite of soda, till the pale yellow tint is removed and the lights remain quite white. The pictures thus finished have a pleasing and peculiar effect. [For the other improvements, *vid.* Hunt's *Researches on Light.*]

Various other processes have likewise been devised for taking sun-pictures on paper. Sir John Herschel has obtained some remarkable results with paper washed with solution of ammonio-citrate of iron. Paper thus prepared is very sensitive to light, but the pictures impressed upon it are faint and sometimes scarcely visible: they may however be brought out very strongly and clearly by washing the paper, after exposure to light, with various liquids, *e.g.* a neutral solution of gold (*Chrysotype*)—and various compounds of cyanogen, ferrocyanide of potassium, &c. (*Cyanotype*). These processes will be found fully described in Sir John Herschel's memoirs (*Phil. Trans.* 1842, II, 181, and 1843, I, 1), also in Hunt's *Researches on Light*, pp. 137—149. The latter work likewise contains a detailed account of the action of light on various compounds of silver, also on salts of gold, platinum, mercury, iron, copper, manganese, lead, nickel, tin, cobalt, antimony, and chromium.—The *calotype* process is however the only one which has been brought into actual use for obtaining sun-pictures on paper. ¶

Daguerreotype. A silvered copper plate is carefully polished with pumice-stone, dilute nitric acid, and cotton, and placed in a box at the ordinary temperature over iodine, till the vapours of the iodine have covered it with a yellow film of iodide of silver. It is then placed for some minutes in the camera obscura, which allows the illuminated picture of an object to fall upon the place. (The light which falls on the plate probably separates iodine from the iodide of silver and sets silver free, chiefly on those parts where its action is most intense.) The plate, on which no alteration is perceptible, is now placed in a dark covered box at an angle of 45° over a vessel containing mercury heated to 75° C. (167° Fah.) till the desired shading is produced. (The mercury which rises in vapour does not adhere to the portion of the surface covered with undecomposed iodide of silver, but only to the silver which has been set free by the action of light, with which it forms an amalgam in drops about $\frac{1}{200}$ millimetre in diameter. Lastly, the plate is immersed in a solution of hyposulphite of soda, then washed with hot water and dried. (Daguerre.) —(The hyposulphite of soda dissolves all the iodide of silver; consequently, on those parts of the plate on which the light in the camera obscura has not acted, there remains clean polished silver, which, when the light falls properly upon it, appears black: on the other parts, according to the intensity with which the light has acted on them, there exist various numbers of amalgamated globules, which, by their greater brightness, bring out the contrast of the picture.)—If a plate of silver polished as above be partly covered with paper and exposed to vapour of mercury, the same contrast is seen on removing the paper. (Fyfe.)—If the iodized plate be covered with different coloured glass plates and then introduced into the camera obscura, a perfect picture will be obtained with blue glass, a tolerably good one with yellow, and none at all with red or green. Ammoniuret of copper acts like blue glass, sesqui-chloride of iron like yellow, acetate of copper like green; on the other hand, the red solution of carmine in ammonia gives a faint picture in which the mercury exhibits a red colour. (Hunt.)—Instead of the tedious polishing of the plate with nitric acid and pumice-stone, it may also be gently rubbed with an aqueous solution of iodide of potassium containing a little excess of iodine,

till all the parts are equally attacked, then exposed to the light for some minutes and polished with dry cotton. (Hunt.)—If the plate be exposed to the vapours of chloride, bromide, &c. of iodine, instead of those of pure iodine, it requires but a few seconds' illumination in the camera, and thus becomes adapted for taking portraits. (Berres.)—In order to obtain more distinct shading, Fizeau spreads upon the plate prepared by Daguerre's method, a solution of 1 part of chloride of gold, and 3 parts of hyposulphite of soda in 1000 parts of water, and heats it gently for a minute or two. The gold which is precipitated from the silver imparts a deeper black to it; the mercury which combines with it makes the colour darker and more stable. [*Vid.* also Daguerre, *Pogg.* 62, 80.]

¶ *Thermography.* Moser (*Pogg.* 56, 177) has shown that: *A surface which has been touched by a body in any particular part, acquires the property of precipitating all vapours that may adhere to it or which combine chemically with it on those parts, differently to what it does on the untouched parts.*—Thus, if we write on glass with any substance that will not scratch the surface, and then breathe upon it, the writing becomes visible. Again, on placing coins upon a plate of glass or metal, and allowing them to remain in contact for some hours, no change is visible when they are removed: but by breathing on the plate, or exposing it to any vapour (that of mercury or iodine for instance), beautiful images of the coins are produced. Absolute contact is not necessary for the production of these images: mere proximity is sufficient. The general law of the phenomenon may be thus expressed "*When two bodies are sufficiently approximated, they mutually depict each other.*" Moser attributes this effect to the action of rays of light which are imperceptible to our eyes, and applies to these rays the somewhat paradoxical appellation of "*Invisible Light.*"—Hunt, who has examined these phenomena with great care, finds that to produce good impressions of coins, &c. on metal plates, it is necessary to use *dissimilar metals.* Thus, when a sovereign, a shilling, a large silver medal, and a penny were placed upon a polished copper plate, the plate gently warmed by passing a spirit-lamp under its surface, and when cold exposed to the vapour of mercury, each piece had made its impression,—but those made by the gold and the large medal were the most distinct, the lettering being copied as well as the disc traced out. Impressions of still greater distinctness were obtained when the plate was more strongly heated.

These experiments seem to show that the calorific relations of the metals materially influence the result; and this is more strikingly shown by the following arrangements.—Pieces of blue, red, and orange-coloured glass, also of crown and flint glass, mica, and a square of tracing paper, being laid for half an hour on a plate of copper, the space occupied by the red glass was found to be well marked, that covered by the orange glass was less distinct, but the blue glass left no impression. The shapes of the flint and crown glass were well made out, and a remarkably strong impression left where the crown glass rested on the tracing paper, but the mica had not left any impression. The same glasses, together with a piece of well smoked glass, were placed for half an hour, $\frac{1}{12}$ of an inch *below* a polished plate of copper. Vapour of mercury brought out the image of the smoked glass only.—All these glasses were placed *on* the copper and slightly warmed. The red and smoked glasses gave, after vaporization, equally distinct images: the orange the next: the others

left but faint marks of their forms. Polishing with Tripoli and putty powder would not remove the images of the smoked and red glasses.

The same coloured glasses, &c., were placed, together with a thick piece of charcoal, upon a plate of copper and exposed to fervent sunshine. Mercurial vapour brought out the images in the following order: Smoked glass, crown glass, red glass, mica, orange glass, paper, charcoal, the coin, blue glass,—thus distinctly proving that the only rays which had any influence on the metal were the calorific rays. For this reason, Mr. Hunt applies the term *Thermography* to the production of images in this manner.

The thermographic process is applicable to the copying of engravings. An account of the method will be found in Hunt's *Researches on Light*, p. 233. The same work, pp. 219—242, also contains a variety of other interesting details relating to this curious mode of action. [*Vid.* also *Ann. Chem. Pharm.* 48, 164.] ¶

Solar light may be supposed to consist of three kinds of rays,—the *heating*, the *luminous and coloured*, and the *chemical rays*,—the first of which are the least and the last the most refrangible. According to this view, the light of the sun refracted by a prism produces three spectra: in the middle the *light and colour spectrum;* on the one side, the *heat spectrum* with its maximum in the neighbourhood of the red; and on the other, the *chemical spectrum* with its maximum in the neighbourhood of the violet. The rays from the green to the red likewise exhibit chemical action, inasmuch as they impart a somewhat lighter colour to chloride of silver: but on the other hand, they seem to exhibit an action contrary to that of the chemical rays, since they remove the blackening from chloride of silver which has been acted upon by white light, and instantly destroy the power of magnets formed by the action of light.—The assertion of Grotthuss, that blue iodide of starch is most quickly decolorized by yellow and green light, and the blood-red alcoholic solution of sulpho-cyanide of iron by blue and green light (from which he concludes that a ray of coloured light most easily decolorizes substances of opposite hue, and endeavours to impart its own colour to them) requires further examination, inasmuch as it is opposed to the experience of other observers. The same may be said of Sir H. Davy's assertion (*Elem.* 1, 187) that the red ray acts on a mixture of chlorine and hydrogen gases and on wet peroxide of lead, more powerfully than the other coloured rays.

Since the chemical rays of light often cause the separation of oxygen from metals, they have been called *de-oxidizing*, and those towards the red and of the spectrum, *oxidizing* rays; incorrectly however, since the chemical rays also bring about the combination of oxygen with guiacum and colouring matters, of chlorine with hydrogen, &c.

Many of the changes produced by light may also be brought about by slight elevation of temperature; *e.g.* the efflorescence of salts; many by a boiling heat, as the decomposition of most metallic salts dissolved in alcohol or ether (sulpho-cyanide of iron dissolved in alcohol is, according to Grotthuss, but little discoloured by boiling); others again by a temperature of from 150° to 200°, as the combination of chlorine with hydrogen, and the bleaching of coloured fabrics exposed to the air; others also at a red heat, at which light may likewise assist,—as the production of oxide of phosphorus. But in many cases the action of light cannot be replaced by that of heat. Chloride of silver does not blacken even at a red heat,

at which it melts and sublimes. The green parts of plants do not separate oxygen from carbonic acid at any temperature in the absence of light. It is also to be remarked that the rays by which chemical action is produced are not the hottest but the coldest rays in the spectrum. Hence it is only in a few cases that we can adopt the views of Rumford and of Gay-Lussac & Thénard, and attribute the chemical effects of light to the rise of temperature which it produces on coming in contact with ponderable bodies.

2. *Development of Light by Ponderable Substances.*

The development of light is either vivid and attended with considerable rise of temperature—*Fire*—or it is faint and accompanied by little or no development of heat—*Phosphorescence, Luminosity.*

A. Development of Light by the mutual chemical action of Ponderable Bodies.

a. Development of Light as a consequence of actual Chemical Combination.

Many substances whose affinity for each other is considerable,—the elementary bodies therefore most of all (according to Law 2, *a.* p. 144),—develop light and heat at the moment of combination. The element which most frequently develops light and heat in combining with others is oxygen; and the act of its combination with other bodies is preeminently denominated *Combustion.* The body which, next to oxygen, most commonly produces light and heat in combining with others, is chlorine; next follow bromine and iodine; then selenium, sulphur, and phosphorus.—But few compound bodies develop light in combining with others.—Hydrate of potash or soda produces light in combining with sulphuric, nitric, or concentrated acetic acid dropt upon it; baryta or lime with water or one of the acids just mentioned; magnesia with sulphuric or nitric acid. (Heinrich.)

The light must either have existed ready formed in one or both of the combining bodies, and be merely separated by the act of combination, or it must be evolved during the combination of the ponderable bodies out of imponderable elements contained in them; on the latter hypothesis, it is most probable that one kind of electricity is supplied by oxygen, chlorine, &c. and the other by the metals and bodies like them. [Vid. *Development of Heat* in the chapter on *Heat,* and *Combustion* in the chapter on *Oxygen.*]

b. Development of Light as a consequence of probable Chemical Combination.

(*a.*) Phosphorescence of living Organized Bodies.

I. *Phosphorescence of Living Animals.*

The phosphorescence of these animals appears to arise from this circumstance,—that they eliminate a peculiar and in most cases liquid substance, containing phosphorus or some other element, which combines, at common temperatures, with the oxygen of the air or of water containing air, producing a faint luminous appearance. Not only does the separation of this fluid appear to depend upon the life of the animal, but its will

seems likewise to determine whether the fluid shall—partly by means of the respiratory process—come in contact with the oxygen of the air, and thus produce a development of light, or not. This view is maintained by Spallanzani, Heinrich, Treviranus, and Tilesius,—whilst Carradori and Macartney regard this luminosity as a consequence of the vital process, and suppose that the increased luminosity in oxygen gas proceeds from augmented vital activity, and the diminution of light in other media from diminished vital energy. But since the liquid retains its luminosity even when separated from the living animals, and the animals often continue luminous even after death, the vital process cannot be the *immediate* cause of the phosphorescence.

The animals which exhibit phosphorescence during life, all belong to the lower classes, principally insects and worms.

Amphibia: The fresh eggs of *Lacerta agilis* (Heinrich), and of some serpents (Langrebe).

Fishes: A peculiar kind of *Leptocephalus.* The bodies of dead fish also appear phosphorescent at times. (Langrebe.)

Insects. 1. *Coleoptera: Elater noctilucus, ignitus, Lampadion, retrospiciens, lucidulus, nictitans, Lucernula, Speculator, Janus, pyrophanus, luminosus, lucens, extinctus, Cucujus, Lucifer,* and *phosphoreus; Lampyris noctiluca, splendidula, Italica,* and *hemiptera* (this according to Illiger is not phosphorescent); *Pausus sphærocerus, Scarabeus phosphoreus* (?) (Luce, *J. Phys.* 44, 300); *Buprestis occellata.*

2. *Orthoptera: Acheta Gryllotalpa.*

3. *Hemiptera. Fulgora laternaria* (the luminosity of which is doubted by Martius and Spix) and *candelaria.*

4. *Diptera: Calex pipiens* (Hablitzl, *Neue nordische Beiträge,* 4, 396).

5. *Myriapoda: Scolopendra electrica, phosphorea* and *morsitans; Julus.*

6. *Arachnidæ: Phalangium.*

7. *Crustacea:* Many *Squillæ; Cancer fulgens, macrourus* and others; *Gammarus Pulex* (sometimes only), *caudisetus, longicornis, truncatus, circinnatus, heteroclitus* and *crassimanus; Oniscus fulgens; Cyclops exiliens; Amymone* and *Nauplius* (the young of *Cyclops*); *Monoculus.*

8. *Annulata: Nereis noctiluca, phosphorans, cirrigera, mucronata, radiata,* and others; *Spirographis Spallanzanii, Lumbricus terrestris, simplicissimus* and *Hirticauda; Planaria retusa; Branchiurus quadripes.*

9. *Mollusca; Pholas Dactylus;* all kinds of *Salpa* (or *Biphora*), as *pinnata, affinis, zonaria, vaginata, bicornis, cornuta, venosa;* and of *Pyrosoma,* viz., *Pyrosoma Atlanticum* or *Telephorus Australis.*

Zoophytes. 1. *Radiata: Asterias noctiluca; Ophiura phosphorea.*

2. *Acalepha*: Very many species of *Medusa,* as *pelagica, pellucens* (these two species perhaps identical), *scintillans, simplex, lucida, hemisphærica, ovata, tuberculata, panopyra, noctiluca, aurita,* the several species of *Aurelia:* many species of *Beroë,* as *fulgens, Pileus, globosa, Brasiliensis, micans, flava; Physalia Arethusa* and *glauca;* several species of *Physsophora,* together with *Rhizophysa* and *Stephanomia.*

3. *Polypi: Sertularia neritina* and *volubilis* (*Qr. J. of Sc. N. S.* 4, 383); *Pennatula phosphorea, grisea,* and all others; *Veretillum Cynomorium,* according to Leuckart; *Isis; Gorgonia; Alcyonium exos,* according to Leuckart; *Spongia.*

4. *Infusoria; Leucophoa echinoides; Trichoda triangularis, granulosa, Clava* and *echinoides; Gleba Pseudohippus, crispa, crystallina, deformis, Conus* and *spiralis; Vorticella; Cercaria: Vibrio; Volvox.*

The eggs of *Lacerta agilis* and of some serpents emit a beautiful green light; the fresher they are, the more brightly they shine. When buried in moderately damp earth, they go on shining for weeks; exposed to the air, they become dry and soon lose their phosphorescence. (Langrebe.) Non-luminous eggs become luminous by agitation. (Gründler, *Naturforscher*, 3, 28.)

In the *Elater*, there are two elongated and roundish luminous spots on each side of the dorsal covering. These are glands containing a yellow substance; and to these the animal, by means of branches proceeding from the cells of the lungs, can allow a large or small quantity of air, or none at all to have access, whereby the development of light is made stronger or weaker, or ceases altogether. The animal shines for six or eight days, even on the needle. (Spex. *Comp.* Illiger, *Mag. d. Ges. naturf. Freunde zu Berlin*. 1807, 141.)

The female of *Lampyris noctiluca* or *splendidula* (the glow-worm), whose abdomen is divided into six segments, shines on the under part of the last three abdominal rings, which are distinguished by a yellowish or greenish white colour from the brown-coloured parts of the rest of the body. Within these three terminal rings is found the luminous matter, a yellowish white transparent substance, consisting of ramifying fibres and granules of an organic structure, heavier than water, yellow and opaque when dry, and consisting principally of a material which exhibits the chemical properties of soluble albumen. (According to Heinrich, an adhesive luminous substance, which imparts its phosphorescent properties to water or oil, may be squeezed out of the animal; according to Macartney, this substance when separated from the animal is no longer luminous, whereas the bag containing the luminous matter shines, when separated from the animal, for several hours in the air, and for 48 hours in water.) The phosphorescence of the animal begins about 7 or 8 o'clock in the evening and continues till sunrise. (According to Macartney, a thermometer rises when placed in contact with the insects while emitting light, but not when in contact with the separated luminous matter of the tail.) The phosphorescence of the insect is totally unaffected by want of food, or by storms, thunder, or candle-light. It is strengthened by repeated gentle disturbance, and is most vivid during the motion of the animal. It is interrupted for a time by sleep, noise, mere violent disturbance, or by cooling to + 12 C° (53·5° Fah.),—and then the phosphorescence ceases from the fore to the back part, two points on the terminal ring often however continuing to glow. The luminous matter, when kept under water, continues to shine for two or three days. If a living worm be placed in water, at 14° C, and the liquid warmed, the animal begins to shine at 27°, emits the strongest light at 41°; continues shining, though dead, at a higher temperature, and its light is extinguished for ever at 57° or 62°. If the temperature of the water be maintained at 35°, the animal continues to shine for a long time after death, but gradually ceases when the water is cooled to 25°. When the insect is warmed without water, the same effect is observed, excepting that the phosphorescence ceases sooner, on account of the drying up of the luminous matter. Dead glow-worms, not yet dry, begin to shine again in water at 44°, and often remain luminous for two or three days after the cooling of the water. Glow-worms killed by cooling them to 0° begin to shine again at 31°. If the head or the luminous ring of a worm which shines of itself be cut off, the light ceases in about five minutes, but re-appears in a few minutes longer in a lower degree, continuing for two or three days, and may be strengthened at

pleasure by warming. The phosphorescence of the extracted luminous matter may likewise be strengthened by moderate heating, and destroyed by a heat of 53°,—in which respect it resembles coagulated albumen. A current of electricity from the electrical machine, or repeated electrical discharges passed through the animal, excite no phosphorescence. If, on the contrary, the insect immersed in a little water be brought by means of two wires within the circuit of the voltaic pile, it instantly becomes luminous and continues so as long as the circuit is complete, but ceases to shine every time the circuit is broken, although the water surrounding the animal shows an elevation of temperature of only $\frac{1}{2}$°. Similar effects are produced upon decapitated glow-worms, on the three terminal rings, and the separated luminous matter, when they are no longer self-luminous.—Neither the animal nor the luminous matter is phosphorescent in vacuo, even at the most favourable temperature or under the influence of the voltaic pile; on admitting the air, the luminosity is restored. The phosphorescence of the luminous matter likewise ceases under oil, probably because the access of air is impeded. In oxygen gas and nitrous oxide, the glow-worm appears to shine somewhat more brightly than in common air. (The increased luminosity in oxygen gas was observed by Spallanzani (*Gilb.* 1, 33) and by Forster. According to Grotthuss, the animals must be cooled some degrees lower in oxygen gas than in common air before they lose their phosphorescence.) In chlorine gas the animal dies instantly, and if subsequently warmed, emits a rose-coloured light for a short time. In hydrogen, carbonic acid, carburetted hydrogen, or sulphurous acid gas, the glow-worm soon dies and emits no light when warmed. According to Spallanzani, also, the light is extinguished gradually in nitrogen and hydrogen gas and instantly in carbonic acid. The luminous matter also loses its phosphorescence in these gases, and shines again on the admission of air or oxygen gas, excepting when the luminosity has been destroyed by chlorine, sulphurous acid, or vapour of hypo-nitric acid.—Alcohol and very dilute mineral acids, which do not kill the animal instantly, cause the final extinction of its light when under water, and likewise of that of the extracted luminous matter; concentrated acids extinguish it instantly. By these means, as well as by heating, or by the action of copper-salts, corrosive sublimate or ether, the luminous matter passes into the state of coagulated albumen, and then its luminosity is destroyed. In aqueous solution of potash the luminous matter dissolves and loses its illuminating power. (Macaire.)

The *Lampyris* shines both as a perfect insect and also in the larva state, but most powerfully in the nymph state. (De Geer.) The eggs begin to shine faintly in four or six weeks, when the larvæ are developed and on the point of emerging. The females shine with peculiar brightness in the breeding-season and during procreation, cease to shine immediately afterwards, but shine brightly again on the following evening; their light is brightest when they are pregnant, at which time they emit light from their whole bodies with the exception of the head. The males do not shine during procreation. (Langrebe.)

The *Lampyris Italica* shines under water for several hours, under oil for only 20 minutes; it soon loses its phosphorescence when immersed in hydrogen, carbonic acid, or nitric oxide gas, but shines again when brought out into the air, provided luminosity has not been too long interrupted; but in this case the insect shines, even when dead, in hyponitric acid vapour, emitting a green light which slowly disappears. (Carradori.)

The female of *Lampyris Italica* exhibits the same steady light as that

of the *L. noctiluca*. But the male, whose two hinder abdominal rings are perfectly luminous, exhibits a flashing light, becoming brighter from 45 to 55 times in a minute, in accordance with the number of pulsations in the same interval. The luminous substance is situated immediately on the lower segments of the two hinder abdominal rings, exactly in the position where the pulsation of the dorsal vessel is the strongest. The blood may in this situation strengthen the phosphorescence, in consequence of the lubrication, vital influence, and excess of oxygen which it causes. The luminous matter separated from the animal is white and viscid,—appears under the microscope to consist entirely of small globules, between which are distributed numerous tracheal ramifications,—shines when spread upon glass, with a greenish light, which diminishes and ultimately ceases when the matter becomes dry, but may often be restored by moisture. (Carus.)

In *Pausus*, the antennæ alone emit a feeble light. (Afzelius.)

In *Fulgora*, the light proceeds from the hollow projection situated on the hinder part of the head, and connected with the air-vessels.

Scolopendra shine over the whole body.

The *Nereis* shines most conspicuously when the sea is agitated by the passage of ships and other causes (Spallanzani); its luminous matter may be diffused through water (Treviranus). According to Viviani, the *cirrigera* is the most luminous of all animals inhabiting the Mediterranean.

Lumbricus terrestris sometimes shines in October on the indurated ring. (Brugière, Flaugergues, *J. Phys.* 16, 311; Andouin, *Institut.* 1840, 381.)

Planaria retusa shines uniformly over the whole body. (Viviani).

The *Pholas Dactylus*, boring muscle, also contains a phosphorescent liquid which adheres to everything which it touches and makes it luminous, and may be expressed and mixed with water, oil, or milk, so as to form a luminous fluid. The boring muscle not only shines externally, but likewise internally when cut open; it continues to shine for a day or two after death, till it putrefies. Its light shows itself between 0° and 56°; gentle heating strengthens it but shortens its duration; stronger heating destroys it. The phosphorescence of muscles becomes brighter in dilute solutions of common salt, nitre, potash, and sugar; it is destroyed by sulphuric acid, vinegar, alcohol, and urine, and by concentrated solutions of potash, sal-ammoniac, salts of lead, and vitriol. Dried pholades recover their luminosity on being moistened with water, even after the lapse of several months. (Beccaria, *Comment. Bonon.* 2, 1, 248.)

Salpæ (according to Edw. Forbes, *Ann. and Mag. of Nat. Hist.*, 1841, 7, 350) do not shine of themselves, but only in consequence of luminous crustacea which frequently adhere to them.

Pyrosoma Atlanticum diffuses a very vivid light, and is often so abundant in the sea that fish can be distinguished by its light at the depth of 15 feet. The temperature of water in which this animal is immersed rises about 1° C., as is likewise the case with Salpæ. (Kuhl, *Schw.* 34, 364.)

The light of Asterias noctiluca spreads itself out from the centre into the rays: the separated rays and their fragments also continue luminous for a time. (Viviani.)

The luminous parts of the Medusæ observed by Spallanzani are: the large tentacula, the edge of the umbella, and the sac which is connected with the opening of the umbella. These parts contain the luminous principle in the form of a thickish glutinous liquid, very different from the

saline watery fluid into which the medusa almost entirely melts when removed from the water. This viscid liquid produces itching when applied to the skin, as does also the juice of several non-luminous medusæ. The luminous matter may be scraped off—renders bodies smeared with it phosphorescent—and when mixed with water, urine, and particularly with milk, forms mixtures which remain luminous for several hours—are increased in brightness by agitation or by warming to 37° C.—may be again rendered luminous after their phosphorescence has ceased—but when strongly heated, are deprived of their luminosity for ever. (Luminous fluids of this kind may also be obtained by mashing up the entire animal in water; if sea-water is used for the purpose, the mixture shines but feebly.)—The medusa shines in water like a torch, so brightly that it can be seen at the distance of 100 paces. Its light is most brilliant when the alternate contraction and enlargement of the disc succeed each other with the greatest rapidity; the light is also strengthened by motion from without. With the diminution of this oscillation the light becomes fainter, and when it ceases, there remains only a very faint luminosity, which may also be observed after death, and does not disappear till putrefaction sets in; it is likewise increased for a time by rubbing. A medusa which has died out of water, and is no longer luminous but beginning to deliquesce, recovers its luminosity in fresh, but not in sea water: the water also becomes luminous. (Spallanzani.)

The luminosity of *Medusa lucida* in water is increased by warming, till the water becomes so hot as to kill the animal. In alcohol it shines still more brightly, but soon dies and ceases to be luminous. Placed in water under an exhausted receiver, it shines as strongly as under the ordinary pressure of the air. The electric spark seems to have no action upon it; electric shocks cause the light to disappear for an instant, but it immediately reappears with increased brightness. (Macartney.)

In *Aurelia*, the light proceeds from the base of the tentacula; in *Beroë* from the vessels under the laced filaments. (Edw. Forbes.)

If a *Physalia* be immersed in alcohol it instantly ceases to shine, because it dies.—*Zoophytes* do not shine when at rest, but only after exertion, and consequently increased respiration, inasmuch as locomotion and respiration are with these animals one and the same movement. Their light becomes fainter as their vital force diminishes, and ceases with their death. This takes place after often repeated exertion and luminosity thence resulting. (Tilesius.)

In the *Pennatula phosphorea*, the light proceeds, not from the stem, but only from the feather,—and is excited only by motion, either spontaneous or induced from without. After death, luminosity is produced by touching the animal, a luminous slime being at the same time expressed from the feather. (Spallanzani.)

In *Alcyonum exos*, likewise, the phosphorescence exists not in the stem, but in the individual polypi. (Leuckardt.)

The phosphorescence of the sea at night—which sometimes diffuses a universal but dull glimmer of light, sometimes presents a fiery surface, at other times shines only in places where it is set in motion by ships or oars, at others again exhibits single sparks, stars, balls, chains, or bands of fire—is mainly attributable to small luminous animals which inhabit the sea. The separate luminous spots are produced by the larger Medusæ, Salpæ, and Pyrosomæ, which emit the most vivid light. (Tilesius.) The general luminosity of the sea is produced by various animals, but more especially by small crustacea whose light is of a sparkling character, by

Nereids, and great numbers of small Medusæ. When sea-water of this nature is filtered, the luminous matter remains on the filter. (Sparmann, Tilesius.) Water taken out of the brightly-shining sea near Martinique gave no light when at rest; on blowing upon it, small bodies crossed the liquid in all directions, shining the brighter the more strongly the surface was blown upon. When stirred, the water became luminous throughout: on being warmed to 35° C. it also became brightly phosphorescent; but when further heated to 43°, its luminosity was completely destroyed. Hydrochloric, sulphuric, and nitric acid, ammonia, carbonate of potash, and alcohol likewise produced a sudden and generally evanescent light. The water after passing through a filter could no longer be rendered luminous: there remained on the filter a number of small animals discernible by the microscope, and consisting of a globule having a yellow spot and a tail, which they moved with great rapidity. (Artaud.)—Moreover, the phosphorescence of the sea is probably often produced by the luminous putrefaction of marine animals, by insolation (as appears to be the case from an experiment of Hellwig), and by electricity, as supposed by Rivière, Le Gentil, and Bajon.

Instances have been known of men whose perspiration is adhesive and phosphorescent, so that the phosphorescence is communicated to their linen; the smell of this perspiration, in the case of an individual of gouty diathesis, in whom the perspiration broke out after violent dancing, was urinous and sour (Henkel, *Crell. N. Chem. Archiv.* 2, 291); in another it had a peculiar phosphoric odour. (Hermstadt, *Magaz. naturf. F.* 2, 248.) Horses in the sweating condition sometimes emit light. Percy saw the wounds on a soldier's thigh continue phosphorescent for fourteen days; over the wounds of another, he saw a light like an ignis fatuus hover for six days. More frequently human urine just voided exhibits phosphorescence. (Jurine, Driessen, *Gilb.* 49, 291; 59, 262.)—Esser (*Kastn. Archiv.* 8, 414) saw the urine which he voided against the wall, when tired after a walk, exhibit phosphorescence; the wall shone for half a minute as if it had been smeared with phosphorus: the urine discharged two hours later was not phosphorescent. The urine of *Viverra Putorius* and *Mephitis* is likewise said to be luminous at the moment at which these animals void it. (F. D'Azora, Langsdorff.) The luminosity of the eyes of animals is due merely to reflected light. (Esser, *Kastn. Archiv.* 8, 399.)

II. *Phosphorescence of Living Plants.*

1. *Sudden emission of Light.*

A sudden flashing light is often emitted, on fine summer evenings, a little after sunset, by certain yellow flowers.

Such is the case with *Tropaeolum majus*, *Tagetes patula* and *erecta*, *Calendula officinalis*, *Helianthus annuus*, *Lilium bulbiferum* and *Chalcedonicum*, *Polyanthes tuberosa*, *Oenothera biennis* and *Gorteria ringens*: likewise *Papaver orientale*. (Elis. Linné, *Abhandl. d. Schwed. Akad.* 24, 291.—Haggren, *N. Abhandl. d. Schwed. Akad.* 9, 59.—Johnson, *Schw.* 31, 361.—Pursch, *Flor. Amer, Septentr.* 1, 261.—Green, *J. Pharm.* 18, 256.) Of these, *Calendula* emits the strongest light; then follows *Tropaeolum*, then *Lilium bulbiferum* and *Tagetes patula*, then *Helianthus* and *Garteria*. The same flower often gives out repeated flashes at intervals of several minutes. This light is undoubtedly electrical, perhaps

produced by the bursting of the pollen granules at the moment of fructification. (Zavadsky.) Ingenhouss, Senebier, and Saussure never observed this luminous appearance in *Trapaeolum majus;* neither could L. Treviranus discover it in *Tagetes* and other flowers; hence he regards the phenomenon as a mere illusion produced by the yellow colour of the flowers, which at night gives them an appearance of peculiar brightness.

Of a different nature from this is the flame observed by Ingenhouss, Bertholon, and Willdenow around the flowers of *Dictamnus albus* on the approach of a lighted candle—an appearance however which Schrank, Th. Saussure, Sprengel, and Treviranus were never able to discover. Biot (*Ann. Chim. Phys.* 50, 386) attributes this flame to the combustion of a volatile oil contained in the cells of the flower-stalks.

2. *Steady Phosphorescence.*

Some plants emit in the dark a faint continuous light, probably resulting from the formation of some substance which burns and emits light at ordinary temperatures, and consists, not of phosphorus, but more probably of a compound containing carbon and hydrogen.

The leaves of *Phytolacea decandra* have been observed to shine in September from 9 till 12 o'clock at night, sometimes with bluish green, sometimes with yellowish green light, accordingly as the current of air was stronger or weaker: they also remained luminous after being wiped. (K. v. Szäts *A. Tr.* 8, 2, 54.)

The acrid, milky juice of *Cipó de Cananam* (a plant growing in Brazil and probably belonging to the genus Euphorbia) emits light for several seconds when it flows from a wound in the plant. (Mornay, *Gilb.* 56, 367.)

Rhizomorpha subterranea stellata and *aidalea*, which grow in mines, emit light from their whole surfaces, but especially from the whitish growing points. The luminosity is brighter in young plants than in old ones; brighter also when they grow in warm, damp parts of the mine than in dry, cold situations: it is also increased when the plants are heated to 40° C. Rhizomorphs shine more brightly in oxygen gas than in common air. When they are immersed in this gas, together with a little water, they often continue luminous for nine days; and the oxygen gas is then found to be nearly consumed and converted into a somewhat smaller volume of carbonic acid. When these plants in the moist state have ceased to shine in the air, their luminosity cannot be restored by electric sparks or by oxygen gas: but it may often be restored by moistening the plant, when its cessation has been caused by dryness. The phosphorescence ceases in vacuo, but reappears when the air is admitted, even if the plant has remained in the vacuum for two hours. The plant likewise ceases to shine when placed in nitrogen gas, but regains its luminosity on being brought out into the air. In hydrogen, carbonic oxide, or chlorine gas, on the contrary, it loses its luminosity for ever, so that no light is emitted even when the plant is afterwards immersed in oxygen gas. (Bischof: *Comp. Schw.* 44, 65; also Laroche, *Verh. d. Ges. naturf. Fr.* Berlin, 1824, 1, 22.)

Rhizomorpha pinnata has been seen by Friesleben to emit light.

According to Linnæus, light is emitted by *Byssus phosphorea* (L) or *Dematium violaceum*. Pers.

According to Funk and Brandenburg, *Schistostega osmundacea*, a plant which grows in caverns, is phosphorescent. This is supposed by

Von Esenbeck to be the same moss which Gilbert (Gilb. 30, 242) saw shining with an emerald-green coloured light in a cavern in the Hartz.

According to Ducluzeau, many confervæ growing near Montpelier are phosphorescent.

(*b.*) Phosphorescence of Putrefying Organic Bodies.

Many organic bodies emit light after death, sometimes before the commencement of actual putrefaction, sometimes simultaneously with it.

1. *Phosphorescence of Putrefying Animals.*

At a certain temperature, and in contact with moisture and oxygen gas, a decomposition appears to arise in many dead animals, especially in sea-fish, before the commencement of actual putrefaction,—producing a glutinous substance, whose constituents are capable of burning in the smallest quantity of oxygen, with a feeble light and scarcely perceptible development of heat:—or may it not be supposed that the decomposition is attended by the production of luminous infusoria?

Human corpses are very rarely phosphorescent. Of a body received on the 14th of February and dissected, one of the lower extremities, which remained over, began to exhibit phosphorescence on the 3rd of March. A second body brought into the same dissecting-room on the 5th of March likewise appeared luminous after a few days, first on the external and internal surface of the thorax, then on the abdomen, bones, tendons, and membranes, more faintly on the muscles, not at all on the viscera of the thorax. A portion of this second body laid upon a third rendered this also phosphorescent in two days, as if by contagion. The luminous matter, which appeared to be of an oily nature, could be removed in many places by the finger, on which it continued to shine. Placed under the microscope, it illuminated the whole field of view, and appeared to be in motion, like gamboge touched with water; but no animalcules were visible, excepting a minute Vibrio, such as is often observed in macerated bodies. The luminous substance continued to shine brightly in oxygen, carbonic oxide, phosphuretted hydrogen, and nitrogen gas—more faintly in carbonic acid—also with various degrees of brightness under water, milk and oil,—lost its phosphorescent power in a vacuum, but recovered it when the air was re-admitted,—and was finally extinguished in sulphuretted hydrogen and chlorine gas, hot air, boiling water and alcohol. (A. Cooper and Appleton.)

Phosphorescence has likewise been observed in the flesh of oxen, calves, wethers, lambs, pigs, fowls, eagles, swallows, and serpents (Fabr. ab. Aquapendente, Boyle, Beale): in the case of ox-flesh, the phosphorescence ceased when actual putrefaction set in. (Bartholinus.) At Orleans in 1780, all the meat in a butcher's shop became phosphorescent. Veal, in October, three days old, cut up and beaten soft, but not yet stinking, emitted at a temperature between 12° and 18° C. a white light like phosphorus—was covered with a glutinous substance—imparted its luminous property to the fingers for a short time—continued to shine 24 hours later, at which time it began to smell badly—and even retained its luminosity, though feebly and only in particular places, after 48 hours, when the stench was much more powerful. (Buchner.)—Hen's eggs have also, on one occasion, been seen to emit light when opened.

Hulme produced phosphorescence in some very young tadpoles by preserving them in a solution of common salt and sulphate of soda.

Phosphorescence is also exhibited by *Sepia officinalis*, *Loligo*, and other species (in *Sepia off.*, according to Spallanzani, the light does not attain its greatest intensity till putrefaction is completely set up);—according to Leuckart, by dead *Aplysiæ*, various species of *Doris* and *Holothuria*; according to Tiedemann, by dead sea-stars; according to Redi, by a *Taenia*; according to Redi, Spallanzani and Tilesius by medusas 24 hours after death; and according to an observation of Leo Allatius, by the refuse of dead crabs.

Luminosity is most readily exhibited by sea-fish, viz. *Squalus Spinax* and *Pristis*; *Tetrodon Mola*; *Muraena Helena*; *Gadus Aeglefinus*; *Morhua Merlangus* and *virens*; *Coryphaena Hippurus*; *Cottus Scorpius* and *cataphractus*; *Pleuronectes Platessa*; *Scomber Scomber* and *Pelamis*; *Perca marina*; *Trigla volitans*; *Clupea Harengas*; *Salmo Salar* and *Trutta*. Freshwater fish may, with some difficulty, be made to emit light, by rubbing them with salt and laying them in a moderately warm place. Heinrich, after many fruitless attempts, succeeded by this process in making the *Esox lucius* emit a very beautiful light, and the *Silurus Glanis* a faint light.

Phosphorescence shows itself in a day or two after the death of the fish, provided they are kept, neither boiled nor salted, in a moist condition, at a temperature of about 12° to 18° C. and in contact with air or oxygen gas. On the contrary, no phosphorescence is produced either in carbonic acid or sulphuretted hydrogen gas, or again when the fish are kept from contact of air by packing—in which case they may in winter be brought to the phosphorescent state by exposure to the air after they have been kept for fourteen days; *e. g.* Shell-fish. (Henrich.)

Phosphorescence begins at the head of the fish, particularly about the eyes, then extends to the belly, and lastly to the tail. (Martin, *Schwed. Abhandl.* 23, 224.) According to Dessaignes, the luminosity is most conspicuous on the aponeuroses, ligaments, capsules, and milts,—in short on the gelatinous parts, not on those of muscular structure. The internal parts do not emit light till they have been exposed to the air for a time. Sometimes there exudes from the animals a glutinous liquid, which is at first clear, but afterwards becomes thick and turbid, and then luminous. (Dessaignes.) This luminous slime may be spread upon the fingers and other foreign bodies. Hulme made a luminous solution of this substance in fresh water, sea-water, or a dilute solution of common salt, Glauber's salt, or sulphate of magnesia, by immersing the flesh of herrings or whitings in these liquids; after three days a luminous ring formed on the surface; when agitated, the whole mass of liquid became phosphorescent, and often continued so for several days.

According to Hulme, no rise of temperature is observable during the phosphorescence. According to Dessaignes, the phenomenon is accompanied by formation of carbonic acid in the air.

A freezing temperature interrupts the phosphorescence; a slight rise of temperature increases it; a boiling heat destroys it for ever. (Hulme.) —Abstraction of water destroys the luminosity of the fish; *e. g.* if it be suspended in a vessel containing quick lime. (Dessaignes.) The action of saturated solutions of various salts, alkalis, sulphuret of potassium, acids, alcohol, and ether may perhaps be similar; nevertheless, their light-destroying power may also proceed from another cause—since dilute acids, even carbonic and hydrosulphuric acid, and likewise lime-water, destroy the phosphorescence. (Hulme.) The luminosity is increased in intensity, but shortened in duration, by dilute solutions of common salt, Glauber's

salt, phosphate of soda, sulphate of magnesia, nitre, sugar, and honey. (Hulme.) According to Hulme, a luminous fish diminishes in brightness when placed in a vacuum; according to Dessaignes, it ceases to shine in vacuo, but regains its luminosity when the air is re-admitted. In nitrogen, hydrogen, carbonic acid, and sulphuretted hydrogen gas, the fish continues to shine for a short time only. (Dessaignes, Hulme.) In boiled water or sea-water, it soon ceases to shine when the air is kept from it; but if air-bubbles make their appearance, the phosphorescence re-appears, and continues for a time proportionate to the quantity of air present. In ordinary fat oil, the fish continues to shine for 24 hours: but if the oil has been boiled, the light ceases as soon as the fish is put into it. (Dessaignes.)

The fish, when left to itself, continues phosphorescent for some days until fetid putrefaction ensues, and then the light disappears.

2. *Phosphorescence of Putrefying Plants.*

The complete decay of the various parts of a plant is also—when the temperature is moderate, and moisture and a small quantity of air are present—at times accompanied by a peculiar decomposition, resulting in the development of a substance which, like phosphorus, burns at ordinary temperatures, producing light and a small quantity of heat. Nevertheless, this substance cannot be phosphorus (especially in wood which does not contain that element), but must rather be considered as a peculiar, and easily combustible compound of carbon, hydrogen, and oxygen, resulting from the decomposition of the original proximate constituents of the plant.

The phosphorescence is chiefly conspicuous in wood, as well in that of the root, as in that of the stem and branches. The phosphorescence has been observed in the wood of *Quercus Robur; Fagus Castanea* and *sylvatica; Betula alba* and *Alnus; Corylus Avellana; Pinus Abies, Strobus, picea* and *sylvestris; Juglans regia;* and some species of willow.

The decomposition of the wood must take place in a situation where but a moderate quantity of moisture is present, and the air is almost excluded, in which case, the wood will remain white; when there is much moisture and free access of air, it is reduced to a brown pulverulent mass which is not luminous. Phosphorescent wood is often but little decomposed, and retains a great deal of its hardness. (Heinrich.) John (*Schw.* 14, 415) saw light emitted by splinters of wood from a newly felled pine. Old wooden pipes often exhibit phosphorescence when taken out of the ground. When roots, which have been dead for some years, are taken out of the earth and kept in a moderately damp place, they often become phosphorescent after a few days. (Heinrich.)—According to Dessaignes, the phosphorescence ceases when the temperature falls to + 6° C (42·8° Fah.); according to Heinrich, it shows itself even at 0° C. fainter indeed, but more durable, continuing for more than fifteen days. By boiling water it is irrecoverably destroyed. Wood heated in the air to the boiling point of water recovers its luminosity by immersion in cold water. (Heinrich.) Wood loses its phosphorescent properties by drying; wood which when exposed to the air ceases to emit light after two or three days, remains luminous for fourteen days when wrapped up in moist blotting-paper (Heinrich). In a vessel containing quick-lime it soon ceases to shine (Dessaignes); but by moderately wetting it, the phosphorescence may to a certain extent be restored.

Wood does not shine for a longer time or with greater intensity in oxyen gas than in common air (Heinrich, Dessaignes); according to Böckman and Gärtner, it does not shine more brightly but longer; according to Spallanzani, it shines with greater brightness. According to Dessaignes, the phosphorescence is brighter, but of shorter duration in compressed air. The same observer found that the phosphorescence gradually died away in a vacuum. Heinrich could not produce any decrease of luminosity by rarefying the air. In nitrogen, hydrogen, and phosphuretted hydrogen gas, the wood remains luminous for only a few hours, and then, according to Spallanzani, recovers its luminosity on the re-admission of common air; in fluoride of silicon, chlorine, ammonia, hydrochloric acid, carbonic acid, and sulphuretted hydrogen gas, its phosphorescence ceases in a few minutes, and cannot be wholly restored by contact of air. (Böckmann, Gärtner, Heinrich.)—In unboiled water, fat oil, and mercury, the phosphorescence ceases after an interval varying from 6 to 24 hours; sooner in alcohol, ether, boiled oil, lime-water, solution of sulphuret of potassium, dilute acids, and saline solutions; instantly in sulphuric acid. Saturated solutions of sal-ammoniac, nitre, and common salt, produce at first an increase of luminosity. (Gärtner, Heinrich, Dessaignes.)

The phosphorescence of wood in air or oxygen gas is attended with consumption of oxygen and production of carbonic acid without perceptible diminution of volume. (Dessaignes.) Air pumped out of decaying wood contains a little oxygen with a great deal of carbonic acid gas. (Dessaignes.) Hence may be explained the fact that wood continues to emit light, even in media which contain no oxygen, provided they do not exert a destructive action on the phosphorescent matter.

Potatoes kept in a cellar till they began to germinate, were, in one instance, observed to emit light on being cut open. (*J. Phys.* 33, 225; also *Gren. J. d. Phys.* 2, 420.)—Kortum (Voigt, *n. Nag.* 2. 67) frequently observed phosphorescence in valerian roots while yet tolerably fresh.—Fresh tormentilla roots gathered in August have been seen to emit light, particularly on those parts where the last year's nodosities were situated. (*Berl. Jahrb.* 1, 174.)—Likewise gourds, mushrooms, and turf are said to be sometimes phosphorescent.

Göbel (*Schw.* 40, 257) allowed some raspberry juice mixed with sugar to ferment in a cask, into the bung-hole of which was inserted a glass tube 1 inch wide and 3 feet long, filled with the same juice, so that the carbonic acid gas developed by the fermentation was compelled to escape through the tube. The bubbles of gas which thus ascended continued to exhibit phosphorescence for more than an hour. The light of the bubbles was strongest just as they passed from the cask into the tube, diminished in intensity as they ascended, and disappeared completely when they came in contact with the air. When the gas was collected by means of a gas-delivery tube adapted to the tube above mentioned, it was no longer phosphorescent, had no smell, and exhibited with ammonia the reaction of pure carbonic acid. (Göbel and Schweigger suggest that the development of light in this experiment may be due to electricity: but it is possible that the carbonic acid gas may have been mixed with a very small quantity of a volatile and combustible organic matter produced by the fermentation, and that this substance may have been burnt with development of light, by combining with the oxygen of the air probably held in solution by the juice of the tube, before the bubbles reached the top of the tube.)

B. Development of Light unaccompanied by any alteration in the Ponderable Matter of Bodies.

a. Development of Light after exposure to Light.

A great number of bodies have the property of shining in the dark when they have previously been exposed to light: such bodies are said to exhibit phosphorescence by *Insolation* or *Irradiation*. The cause of this phenomenon is probably that the bodies, by being exposed to light, absorb a portion of it unaltered into their substance by adhesion, and subsequently give it out in a dark place,—because there the effort of the light to diffuse itself uniformly through the space devoid of light overcomes its adhesion to the ponderable matter.

Phosphori by Irradiation, Light-absorbers, Light-magnets, are transparent or opaque, colourless or slightly coloured, but never black substances.

The best phosphori by Irradiation are the following: Diamond (some diamonds however have no phosphorescence.) (*Heinrich.*)

Bononian Phosphorus. (1.) A paste made of gum tragacanth and powdered heavy spar free from iron and dried, is placed in layers between small coals in a wind-furnace (or in a crucible,—*Wach*) ignited for an hour, and transferred while yet warm into well stopped glass vessels. (John.) 3 or 4 per cent of magnesia mixed with the powdered heavy spar improves the phosphorescence considerably. (Wach.) (2.) Osann passes hydrogen gas over sulphate of baryta heated to redness in a tube. (3.) Daguerre fills a marrow-bone, as thick as can be procured, freed from fat and dried, with heavy spar pounded in a non-metallic mortar—lutes it—incloses it in a tube of iron-plate or cast-iron—surrounds and covers it completely with fire-clay—exposes the whole to a red heat in the furnace for at least three hours,—then removes the clay from the bone (which should be white after cooling,—a grey colour would show that it had not been heated long enough), breaks it up on paper—and preserves the white or pale yellow phosphorus thus obtained. If it be heated once or twice more in a fresh bone, its phosphorescent properties will be greatly increased. The sulphate of baryta used must be perfectly free from iron and other heavy metals.

Strontian Phosphorus may be prepared in a similar manner (1) from cœlestin (John): its luminosity may be greatly increased by the addition of 3 or 4 per cent. of magnesia to the powdered cœlestin.

Canton's Posphorus. (1.) Canton exposes a mixture of 3 parts of sifted and calcined oyster-shells and 1 part of flowers of sulphur to a strong fire for an hour. (2.) Grotthuss places oyster-shells—which have been previously cleaned and ignited by themselves for half an hour—in alternate layers with pounded sulphur in a crucible, the inner surfaces of the shells being turned downwards,—and heats the crucible in a wind-furnace for at least an hour. The oyster-shells must be previously well burnt so as to remove all dark spots, and their inner surfaces must be cleaned from adhering ashes with a soft brush which will not injure them. The phosphorus is more luminous when the burnt oyster-shells are heated with sulphur in their entire state than when they are pounded. Moderate ignition for half an hour in contact with sulphur is generally quite sufficient: more powerful and longer-sustained ignition produces a phosphorus which is but faintly luminous. Pure lime heated with sul-

phur yields a much weaker phosphorus than that produced from oyster-shells, because the latter contain a little magnesia. (Wach.) (3.) Dessaignes ignites gypsum mixed with flour.

Osann's Phosphori.—*a. Antimonial Phosphorus:* Formed by placing cleaned and ignited oyster-shells in alternate layers with finely pounded sulphuret of antimony in a well covered crucible, and heating the mixture for an hour: after cooling, the white pieces are to be picked out, the yellow and black ones thrown away.—*b. Realgar Phosphorus:* The same mode of preparation, but using realgar instead of sulphuret of antimony.—*c. Arsenical Phosphorus:* A paste formed of neutral arseniate of baryta and gum tragacanth is dried and ignited for half an hour between coals or on an earthenware support: it has a greyish yellow colour.—*d.* Burnt oyster-shells treated as in *a* with orpiment instead of sulphuret of antimony, or—*e.* with mosaic gold, or—*f.* with cinnabar, or—*g.* with a mixture of sulphur and zinc-blende, or—*h.* with arsenious acid. Of all these phosphorescent compounds, the most luminous are *a*, *b*, and *c*.

Wach's Phosphori: a. Burnt oyster-shells thinly sprinkled with solution of artificial tersulphuret of arsenic, covered after drying with pounded sulphur, and ignited in a covered crucible, produce an excellent phosphorus.—*b.* Three parts of burnt oyster-shells disposed in alternate layers with 1 part of a mixture of 10 parts of flowers of sulphur and 1 part of oxide of antimony, and moderately heated in a covered crucible.—*c.* Similarly with oxide of zinc.—*d.* With oxide of cadmium.—*e.* With peroxide of tin.—*f.* A solution of arseniate of ammonia is dropped upon calcined oyster-shells, which are then sprinkled with sulphur and ignited.—Similarly with chloride of antimony—*h.* With sulphate of zinc.—*i.* With sulphate of cadmium.—*k.* With proto-chloride of tin.—*l.* Good phosphori are likewise obtained by igniting hyposulphite or sulphite of baryta, strontia, or lime, particularly hyposulphite of lime mixed with 3 or 4 per cent. of magnesia.

Lastly, among good phosphori may be enumerated: *Homberg's Phosphorus* (chloride of calcium, which Homberg formed by melting 1 part of sal-ammoniac with 2 parts of slaked lime); *Baldwin's Phosphorus* (nitrate of lime fused till the nitric acid begins to decompose); many kinds of fluor-spar, as the chlorophane of Nertschinsk (Grotthuss), and a variety of fluor-spar from Dauuria (*Schw.* 49, 259); strontianite; arragonite; calcspar; marble; stalactites; chalk, and slightly-burnt oyster-shells.

Less powerfully luminous, according to Heinrich, are: Crystallized boracic acid, sal-ammoniac, sulphate of potash, nitre, crystallized carbonate, borate, and sulphate of soda: rock-salt, witherite, radiating heavy spar from Bologna, marienglas, fibrous gypsum, alabaster, artificial sulphate of lime, (common fluor-spar—*Grotthuss*), crystallized sulphate of magnesia, crystallized alum, arsenious acid, pharmacolite, freshly prepared flowers of zinc, sulphate of mercury, tartar, benzoic acid, loaf-sugar, sugar of milk, bleached wax, white paper (especially when it has been heated almost to burning: yellow and red paper are nearly as phosphorescent as white, dark blue paper is not at all so—(*Grotthuss*); egg-shells, corals, snails, pearls, bones, teeth, ivory, leather, and skins of men and animals.

The following are phosphorescent in a tolerably high degree: Tartaric acid; also seeds, grain flour, starch, crums of bread, gum-arabic, feathers, cheese, yolk of egg, muscular flesh, tendons, isinglass, glue, horn—all well dried; moreover, the alburnum of trees, bleached linen, bleached cotton-yarn, and other bleached vegetable fibres.

Moderately phosphorescent are: Ice, oxide of antimony, sulphate of zinc, white lead, iron pyrites, alum-slate, basalt, potter's clay, fuller's earth, bark of trees, amber.

Feebly luminous are: Cœlestin, smalt, magnetic iron ore, red ochre, undried seeds, flour, and starch; also, according to Grotthuss, blue carbonate of copper (*Kupfer-lazur*), and beryl.

Very feebly and often not at all luminous are: Glass, silica, rock-crystal, amethyst, cornelian, prase, heliotrope, sapphire, corundum, chrysolite, spinell, emerald, topaz, tourmalin, hyacinth, garnet, melanite, leucite, adularia, common felspar, zeolites and other minerals; chloride of zinc, yellow blende, wood, most kinds of resin and gum, silk, and animal substances not well dried.

The following, according to Heinrich, exhibit no phosphorescence: Water and all other liquids, sulphur, graphite, all metals in the free state, baryta, strontia, lime, apatite, red lead, red oxide of mercury, fresh parts of plants, unbleached yarn of hemp and flax, mineral pitch, fossil tar, coal, jet, turf, charcoal. Moreover, according to Dessaignes, all metallic sulphurets except orpiment.

According to Dessaignes, phosphorescence is also exhibited by: Glucina, phosphorite from Estremadura, orpiment, flowers of sulphuret of antimony (*spiessglanz-blumen*), sulphate and phosphate of lead, protochloride of tin, a mixture of peroxide of tin and oxide of lead, and imperfectly slaked baryta, strontia, and lime.

These bodies will not shine in the dark unless they are first exposed to light: even the Bolognian and Canton's phosphorus, which are prepared by ignition, do not shine when left to cool in the dark and not first exposed to light (John): neither do the realgar and antimonial phosphori, even when heated to 100° C. (Osann.). Most of these bodies require to be exposed to the direct rays of the sun. The Cantonian and Bolognian phosphorus, diamond, paper, chlorophane, sulphate of potash and common salt, are rendered luminous by reflected sunlight; the five substances first named, by strong lamp-light; the Bononian phosphorus, and Osann's phosphori *a*, *b*, *c*, by the light of phosphorus burning in oxygen gas. (Phosphorus burning in oxygen gas under a bell-jar makes Canton's phosphorus but very feebly luminous, because the light passes through the glass—*E. Becquerel.*) The last three phosphori (not the Bolognian) are also rendered phosphorescent by the light of sulphur burning in oxygen gas, and even by the light of a tallow candle, placed at the distance of a foot; the antimonial phosphorus, likewise by the light of white-hot iron at the distance of a foot; (in the last experiment the phosphorus was placed in a dish surrounded with ice); burnt oyster-shells, by the light of burning alcohol impregnated with common salt; Canton's phosphorus and some diamonds are also rendered luminous by moonlight. The intensity of the emitted light is however always proportional to that of the light by which the phosphorescence has been excited. Bodies may be rendered luminous by irradiation, even when immersed in water. (Heinrich, Dessaignes, Osann.)

Canton's phosphorus, after being exposed to daylight for two seconds, exhibits the greatest luminosity when immersed in water: the light appears to be somewhat fainter when the substance is freely exposed to day-light; fainter again when the light falls upon it through a plate of rock-crystal 7 inches thick; still fainter when it passes through blue glass, and faintest of all when the light reaches the phosphorus after passing through a plate of white glass 3 millimetres thick, or through a

sheet of solid gelatine. When the irradiation continues from 10 to 20 seconds, the difference is no longer perceptible. (Biot.)

Of all the coloured rays of the prism the violet (or the blue according to Grotthuss) and the invisible rays beyond the violet act most powerfully in producing phosphorescence. This power diminishes with the refrangibility: according to Heinrich, the red ray does not induce phosphorescence in the diamond; according to Seebeck and Grotthuss, a feeble luminosity is induced by the red ray, and according to Seebeck, by the invisible rays adjoining it. Phosphori which have been rendered luminous by colourless light, cease to shine much sooner in red light than in the dark; and instantaneously when exposed to red light concentrated by a lens. (Seebeck.) Similar opposition of effects is produced by light which has passed through coloured glasses. Light transmitted through blue glass makes Canton's phosphorus almost as luminous as colourless light concentrated by a lens; behind red glass, on the contrary, the phosphorus not only fails to acquire luminosity, but ceases to shine when previously irradiated, much sooner than it would if placed in the dark. (Seebeck.) Osann's phosphori *a*, *b*, and *c* become strongly phosphorescent under colourless, violet, and blue glass, faintly under light green and light yellow, very faintly under orange-coloured, and scarcely or not at all under red glass. (Osann.) Calcined oyster-shells become strongly luminous when exposed to day-light under dark violet glass (which when analysed by the prism appears to consist of violet, blue, and red), very faintly under bluish green, and scarcely at all under homogeneous red glass coloured with suboxide of copper. (Biot and E. Becquerel.) Bolognian phosphorus prepared according to (3), half covered with a plate of blue glass and exposed to sunlight, becomes less luminous in the direct light of the sun than under the blue glass. (Daguerre.) The same result therefore as that obtained by Seebeck. It appears from this that colourless light contains rays which oppose the production of phosphorescence, viz. the orange, as shown by Seebeck. It is therefore the chemical rays of light by which phosphorescence is produced.

Chlorophane, Canton's, and the Bononian phosphorus insolated at a temperature of — 31° C (— 24° Fah.) shine at + 10° C. (50° Fah.), longer and with greater intensity than when they have been exposed to light at + 31° C. (88° Fah.) (Grotthuss). Phosphori newly prepared by ignition and exposed to light while yet hot acquire little or no luminosity; it is only when cool that they are susceptible of the influence of irradiation. (Osann.) Canton's phosphorus insolated at temperatures from 100° to 200° C, and then taken immediately into a dark room exhibits but a feeble light. (E. Becquerel.)

A merely momentary irradiation produces phosphorescence, though but for a short time; longer continued irradiation does not produce stronger or more lasting phosphorescence than irradiation for 10 seconds only. (Dessaignes, Heinrich.) Pulverized phosphori exposed in masses to light, shine afterwards only on the surface, and when stirred with a rod, exhibit dark streaks. (Osann.)

The phosphorescence is sometimes so weak that it can only be perceived by an eye which has been in the dark for a long time; but good phosphori often shine in twilight. Wach's phosphori are visibly phosphorescent even by daylight, and illuminate a dark room.

The duration of the phosphorescence varies greatly according to the nature of the body. Canton's phosphorus, after being exposed to sunshine for 10 seconds, shines for 10 hours according to Dessaignes, and for

5 days according to Grotthuss; chlorophane for 10 days according to Grotthuss, and 30 to 60 minutes according to Heinrich; Bolognian phosphorus prepared by (3), for 48 hours according to Daguerre, 1 hour according to Heinrich, 4 minutes according to Osann, and 80 seconds according to Dessaignes,—realgar phosphorus for some hours, antimonial phosphorus for 149 minutes, arsenical phosphorus for 34 minutes (Osann); diamond from 5 seconds to an hour; common fluor-spar from 1 to 30 minutes, most salts and organic substances from 6 to 20 seconds, minerals for a still shorter time. (Dessaignes.)

The colour of the light varies in an equal degree according to the nature of the substances. Most of them emit a white light, diamond and Bolognian phosphorus a yellowish red,—arsenical phosphorus a yellowish red, when longer ignited a reddish yellow, and after still longer ignition a colourless light,—Canton's phosphorus a light yellow rose-red or pale violet,—phosphori from oyster shells and cinnabar a yellow,—antimonial phosphorus a light green, or, when it has been ignited for a long time, a colourless light,—glucina and chlorophane a green,—strontian phosphorus a green or bluish light,—realgar phosphorus a blue light, in some places yellow and purple red, but after strong ignition a white light,—phosphori from oyster-shells and mosaic gold or blende a bluish,—calcined oyster-shells a red and in some parts a pale blue light. Wach's phosphorus *a* gives a blue, *b* a white, *c* a bright green, bluish in parts, *d* a deep yellow and *e* a white light; the part *f* sprinkled with arseniate of ammonia appears of a fiery red with a green border; that moistened with chloride of antimony *g*, a yellowish red with lighter border; that with white vitriol *h*, a faint light with a bright bluish luminous zone, that moistened with sulphate of cadmium *i*, a bright yellow with bluish circumference; and that sprinkled with chloride of tin *k*, shines with a faint yellowish light surrounded by a luminous border. Since the border generally shines the most brightly, a minimum quantity of metallic salt seems best adapted to strengthen the illuminating power of the phosphorescent body. (Wach.)

This colour bears no relation to that of the light by which the phosphorescence has been developed. Thus diamond or Bolognian phosphorus insolated with the blue or violet ray, shines with yellowish red, and Canton's phosphorus under the same circumstances with light yellow or rose-coloured light. Hence Grotthuss concludes that the phosphorus has the property of converting colourless into coloured, and coloured light into light of another colour or white light; and he considers the differences between the several rays as resulting only from the different velocities of the lateral oscillatory movements of the rays, the direct velocity of propagation being the same for all.

Phosphorescence shows itself in all transparent media which do not alter the composition of the phosphorus; the diamond shines in water, hydrogen gas, nitrogen, and nitrous gas (Heinrich); chlorophane in water (Grotthuss); Canton's phosphorus in a vacuum and in all gases,—but acid gases soon destroy its luminous power, and chlorine destroys it instantly (Dessaignes); similarly in water and alcohol (Grotthuss).

The phosphori formed from realgar and antimony retain their property of shining by insolation, when kept for a long time under water; the former does not shine more brightly in oxygen gas than in common air. (Osann.)

The phosphorescence of these bodies shows itself, according to Heinrich, as strongly at − 12° as at + 25°. A higher temperature

strengthens it but shortens its duration. When a body like Canton's phosphorus or chlorophane has ceased to shine at a certain temperature, it will shine again, even months after, when its temperature is raised, *e. g.* by the warmth of the hand, by boiling water, or the approximation of a hot iron: but it afterwards requires renewed insolation to make it shine again. (Canton, Grotthuss, Osann.) Canton's phosphorus insolated in a freezing mixture and removed to a dark place without being taken out of the mixture, shines as strongly as if it had been insolated and placed in the dark at the ordinary temperature; but after ceasing to shine in the freezing mixture, it again begins to emit light when raised to the ordinary temperature. (E. Becquerel.)—The Bolognian phosphorus prepared according to (3), and spread upon a plate which is carried in the open hand, causes the fingers to show through the plate, because where their warmth is conducted through the plate, the phosphorus shines more brightly. (Daguerre.)

Translucent substances, such as marble, likewise emit light from the surfaces of fractures formed during phosphorescence.

All phosphori retain their phosphorescent properties only so long as they are not chemically altered; hence some of them, such as the Bolognian and Canton's phosphorus, must be preserved in sealed tubes. Some of them, *e. g.* diamond dust, chlorophane, common fluor-spar and sulphate of potash, lose their power by ignition, but recover it when an electric shock is passed through them. (Dessaignes, Grotthuss.)

The effect of insolation in rendering these bodies phosphorescent may be replaced by that of the electric light produced by passing the charge of a jar through them. Canton's phosphorus becomes beautifully luminous when placed in a tube of blue or colourless glass over which an electric charge is passed (in a yellowish red tube no phosphorescence is produced). (Seebeck.) The intensity of the phosphorescence increases up to a certain degree with the strength of the shock; sometimes only a streak of light appears following the course of the spark, sometimes the whole body shines. (Heinrich.) The phosphorescence produced by electricity has the same colour and the same duration as that induced by insolation (Dessaignes); according to Grotthuss it is brighter.—The electric spark produces phosphorescence, not by mechanical disturbance or electric action, but by its light. Canton's phosphorus or green fluor-spar becomes luminous when the spark of an electrical battery having a surface of 2 square mètres is passed over it, at any distance from 1 decimètre to 3 mètres; (at which last distance the electrical effects are no longer perceptible); but the greater the distance, the weaker is the light. Several sparks at a great distance produce as much phosphorescence as one close at hand. If the Cantonian phosphorus exposed to the electric spark be placed under glass coloured red with suboxide of copper or under yellowish green glass, it does not become luminous; under blue glass it becomes very faintly luminous, under violet or colourless glass rather more so (and the thinner the glass the greater is the effect) but not nearly so bright as when it is exposed without any covering to the action of the spark. (E. Becquerel.) Under a plate of rock-crystal, smoky topaz, or gypsum (Marienglas) Canton's phosphorus becomes much more powerfully luminous than under a plate of colourless glass, even of less thickness; the phosphorus also becomes luminous when covered with two plates of rock-crystal with water between them. If it be covered with opaque paper in which there is an aperture 1 millimetre in diameter, and the electric spark passed over this aperture, it will be found, on removing the paper in the dark, that

the phosphorescence is at first confined to a small circle, whence it gradually diffuses itself over the whole phosphorus, then gradually diminishes and disappears. (Biot & E. Becquerel.)

b. Development of Light, produced by the action of Heat.

Almost all bodies which are capable of becoming phosphorescent by insolation and have ceased to shine at ordinary temperatures—and others likewise—become luminous when heated in the dark. It seems therefore that the bodies at the ordinary temperature contain a certain quantity of light so intimately combined with them, that it cannot diffuse itself through a dark space by virtue of its own elasticity; but that the capacity of bodies to fix light diminishes as their temperature rises.

The substances which exhibit phosphorescence when heated are not only almost all those which acquire the same property by insolation, but likewise those diamonds which do not become luminous by insolation (Heinrich); also baryta, strontia, lime, magnesia, alumina, apatite, the filings of several metals (zinc and antimony are the most luminous, gold and silver the least; mercury also exhibits a very faint luminosity according to Dessaignes, none at all according to Heinrich)—very many metallic oxides, both hydrated and anhydrous, almost all earthy minerals, *e. g.*, red sapphire, rock crystal, red felspar, red mica, asbestus, steatite (Wedgewood); wernerite, dipyre, tremolite, harmotome (Hauy); heavy spar, anhydrite, bitterspar, datolite, green sapphire, brown adamantine spar, common quartz, amethyst, grey hornblende, blue, yellow, and white topaz, rubellite, cyanite, spodumene, petalite, sodalite, green, brown, and black mica, lapis-lazuli, obsidian, mesotype, tabular spar, augite, glassy actynolite, sphene, anatase, black titaniferous sand, tungstate of lime, sulphate of lead, arseniate of lead, red silver (Brewster); baryto-calcite. (Children, *Ann. Phil.* 24, 115.)—Sulphate of quinin and sulphate of cinchonin shine when moderately heated; resin of guiacum, mastic, sandarach, olibanum, myrrhs, galbanum, and ammoniacal resin at their boiling points; gum arabic, marsh-mallow root, and Florentine violet-root, at a heat at which they begin to char, perhaps, therefore, in consequence of a slow combustion. (Jonas, *Br. Arch.* 17, 250.) *Comp.* Bottger. p. 200. Likewise wax, fat, and volatile oils, and many other organic bodies, shine when heated, their phosphorescence being, however, due to slow combustion; the same remark applies to the luminosity of the filings of several metals, which may perhaps be due partly to the combustion of the metal, partly to that of oil adhering to it.—The sparkling observed by Döbereiner (*Schw.* 41, 221) on heating chlorate of potash with powdered peroxide of manganese (or with fine quartz-sand) (Schweigger), in a glass tube likewise results from chemical combination.

Phosphorescence is not induced by heating in bodies which fuse or volatilize at a high temperature, *e. g.* the hydrates of potash and soda, nitre, the nitrates of strontia and lime, and ammoniacal salts, which at most become slightly luminous when gently heated (Dessaignes); neither does it occur in incombustible liquids (Heinrich).

The lowest temperature capable of inducing phosphorescence is not only different in different substances, but likewise varies in different specimens of the same substance. With Canton's phosphorus, chlorophane (Pallas), many diamonds, and white topaz (*J. Phys.* 55, 60), which have ceased to shine in the dark at ordinary temperatures, the heat of the hand or the breath,—and with the first mentioned substance, immersion

in oil of vitriol or nitric acid, which produces heat, is sufficient to excite phosphorescence; with common fluor-spar the temperature must be raised to between 63° and 100° C., with phosphorite from Estremadura and adularia to 100°, with diamond between 100° and 250°, with the natural forms of carbonate of lime between 200° and 325°, with minerals of the siliceous class between 250° and 375°, with oils between 94° and 250°. In this respect it is indifferent whether the body is in the form of lumps or powder, and whether the heated support consists of glass, clay, porcelain, iron, copper, silver, mercury, or tin, or whether the substance is thrown into hot water.

Bodies which become strongly phosphorescent by insolation, generally also shine brightly after being heated,—and conversely: a considerable degree of phosphorescence is however acquired by hard minerals when heated. The longer a body shines by insolation, the longer also, generally speaking, does it shine after heating; and with the same body, the phosphorescence produced by heat lasts longer than that excited by insolation, —with the exception of diamond, fluor-spar, Canton's phosphorus, and other bodies, which shine for a long time after insolation, and, on the contrary, for a shorter time after being heated. The intensity of the light is also directly proportional, its duration inversely proportional, to the degree of temperature to which the body is raised.

With most bodies the light is soft and streaming, with metal filings and certain heavy metallic oxides it is sparkling. (Dessaignes.) The colour of the light bears no relation to that of the phosphorescent body, and is more variable than when produced by insolation, being sometimes white, sometimes violet, blue, green, yellow, or reddish: the same body often exhibits several of these colours at different stages of the process of heating, sometimes in the order just mentioned, sometimes in the reverse order, but always in such a manner that some of the colours are passed over. (Heinrich.)—The light emitted may be resolved by the prism into a coloured spectrum, just like ordinary light.

Inorganic bodies shine equally well in common air, oxygen, nitrogen, hydrogen, or carbonic acid gas, or in vacuo, water, or oil; organic substances, on the contrary, shine only in air, or still better in oxygen gas; their phosphorescence is therefore to be regarded as a phenomenon of combustion. Only in the case of linseed oil, Dessaignes was able to distinguish a fainter luminosity, which occurred at 125° C., even in carbonic acid gas, from the stronger phosphorescence which was produced at a higher temperature, and only when oxygen was present. The phosphorescence of boiling linseed oil ceases when the air is removed by the air-pump, and recommences when it is again admitted. (Grotthuss.)—Quinin, sulphate of quinin, and sulphate of cinchonin, do not shine so strongly during the time that they are heated (on paper over a lamp) as they do 30 or 40 seconds after the removal of the lamp: the luminosity begins at the edge, extends towards the middle, and often lasts several minutes. Other salts of quina and other organic salifiable bases exhibit no phosphorescence. (R. Böttger, *Ann. Pharm.* 33, 342.)—Luminous characters may be traced on paper with a piece of iron heated somewhat below redness. The vapour which rises from paper heated by contact with hot iron is also luminous; so likewise are wood and sugar when touched with a hot iron. (Grotthuss.)—The wick of a tallow candle, which has been extinguished in the dark, so as not to leave a single spark alight, remains faintly luminous for some seconds. If sulphur, wax, tallow, fat oil, camphor, resin, or caoutchouc be rubbed upon hot iron not luminous in the

dark—or if the iron be brought in contact with gum, starch, horn, feathers—or if olefiant gas or ether vapour be made to rise against it—a pale, bluish white, lambent flame of various degrees of intensity will be produced. Tallow, paper, and cacao-fat exhibit phosphorescence at 149°, wax not below 204° C. (Williams, *Pogg.* 39, 490; also *J. pr. Ch.*, 6, 92.)

Bodies which have ceased to shine at a certain temperature again become luminous when more strongly heated; but they then require to be once more exposed to light before they will exhibit phosphorescence on being heated. The realgar and antimony phosphori prepared in a covered crucible and cooled in the dark do not become phosphorescent by heat; but if exposed to light and then kept in the dark for a long time, they emit light on being heated. (Osann.)—The application of a very strong heat produces a momentary and very vivid phosphorescence, but deprives most bodies, the heavier metals, their oxides and salts, for example, of the power of again becoming luminous: *e. g.*, metal filings do not emit light when too much pressure has been used in the act of filing. (Dessaignes.)—Many other bodies may be deprived by half an hour's ignition of the power of emitting light when heated, *e. g.*, precious stones, glass, quartz, clay, magnesia, heavy spar, strontianite, carbonate of lime, fluor-spar, and many other salts of the alkalis and earths which partly lose their water of crystallization when ignited. The luminous power is however restored by electric discharges even when sent through a paste formed of the powdered substance mixed with water (this is the case with carbonate of lime, fluor-spar and heavy spar); in the case of salts which have lost their water of crystallization by ignition, the phosphorescent power is restored by exposure to the air, by breathing on them, or moistening them (some salts indeed, after being moistened with water, shine again, though but faintly, when heated, without previous exposure to light, —(Dessaignes, Grotthus); and in the case of strontianite and carbonate of lime, by heating to whiteness (Heinrich, Dessaignes).—Chlorophane, which has lost its phosphorescent properties by ignition, yields, by solution in hydrochloric acid and evaporation, crystals of fluor-spar which acquire little or no luminosity when heated; whereas if the chlorophane be fresh, or if its phosphorescent power after being destroyed by ignition has been restored by the electric spark, it will, when treated by hydrochloric acid, yield crystals which emit light on being heated. If ignited and unignited chlorophane be dissolved in hydrochloric acid and precipitated by ammonia, the precipitate of the former will shine when heated with a faint bluish white light, that of the latter with a bright emerald green light. If the hydrochloric acid solution of unignited chlorophane be treated with sulphuric acid, the precipitated sulphate of lime shines almost as brightly as the chlorophane itself, but with a somewhat different light; if a solution of ordinary chloride of calcium be treated with sulphuric acid, a precipitate of gypsum is obtained which is quite destitute of phosphorescence. (Grotthus.) If ignited chloride of sodium be dissolved in one portion of water, and the same salt ignited and afterwards electrified be dissolved in another portion, and both solutions evaporated, the latter will evaporate more quickly than the former, effloresing at the same time—and yield a salt which shines more brightly when heated than that which evaporates from the former solution. (Grotthuss.) Baryta, strontia, lime, magnesia, alumina, and silica do not lose by ignition the power of emitting light when heated. (Dessaignes.)

Pearsall, in the following experiments, placed the substance to be

examined on ivory, and passed through it one or two shocks from a Leyden jar having a surface of two square feet. He found that the same effect is produced when the spark is passed over the substance inclosed in a glass tube, whereas the vivid light between the charcoal points attached to the terminal wires of a voltaic pile of 100 pairs has no effect whatever. Chlorophane deprived by ignition of the power of emitting light when heated does not recover it by two days' exposure to the sun's rays, but regains it almost entirely by one electric shock (producing a green light) and still more powerfully by repeated shocks. Ordinary fluor spar electrified after ignition shines brightly on being heated, if kept for several weeks in the dark; but if after being electrified, it is exposed to the sun for the whole of this interval, it gives little or no light when heated. Apatite, electrified after ignition, shines with a citron-yellow light. Unignited fluor-spar, which does not shine when heated, acquires this property in a higher degree, the greater the number of electric shocks passed through it. Unignited fluor-spar becomes luminous when heated, emits after the action of electric shocks a more intense light, which, after several discharges have been passed, approaches more nearly to that of chlorophane, and exhibits colours different from those which it had before electrization. Minerals containing silica and alumina and not originally possessing the faculty of emitting light when heated, do not acquire this power by the action of electric shocks. A solution of phosphorescent apatite or fluor-spar in hydrochloric acid gives, when treated with ammonia, a precipitate which does not become luminous when heated, either after simple drying or after ignition and electrization; but a urinary calculus consisting of phosphate of lime becomes luminous when similarly treated. The crystals of fluoride of calcium which the solution of fluor-spar in hydrochloric acid deposits on cooling likewise emit light on being heated. (Pearsall.)

c. Development of Light by Mechanical Force.

Almost all bodies which acquire phosphorescence by insolation or by the action of heat, likewise become luminous by friction or percussion. The combined light thus disengaged from them is probably the same as that which is set free by heat; from which cause also the intensity of the light developed by percussion increases with the temperature.—Becquerel (*Ann. Chim. Phys.* 22, 33) refers the light developed by pressure to electric action: if for example two masses of ice come in contact at sea, they are brought by strong pressure into opposite electrical states;—and when the pressure ceases, the opposite electricities combine again and produce light. The development of light by friction is in many cases undoubtedly of an electric nature, *e. g.*, in that of sulphate of quinin. Moreover, pressure produces heat—and this may excite phosphorescence by rise of temperature. There is probably also, according to Heinrich, a *Light of Separation* (*Trennungs-licht*), *i. e.*, a development of light produced by destruction of cohesion as in splitting, tearing, or breaking; in few cases, *e. g.*, iron pyrites, is the production of light a consequence of combustion. R. Böttger (*Pogg.* 43, 655) endeavours to prove that the light developed by rubbing flints together is electrical—from the fact that, like the electric light, it shows distinctly and separately the colours painted on a revolving circular disc; Doppler (*Pogg.* 49, 505) regards this proof as insufficient.

Solid Bodies.

Phosphorescence produced by tearing, splitting, and rubbing.—When boracic acid solidifies after fusion, it splits in cooling, and exhibits along the cracks a light which is visible even in the daytime. (Dumas, *Ann. Chim. Phys.* 32, 335, also *Pogg.* 7, 535.) Sulphate of potash fused with cream of tartar and a little common salt, likewise cracks in cooling and emits light. (Schiller, *Tascherb.* 1791, 54.) Glass-drops almost always emit light when they burst. (Heinrich.) In the cleavage of Russian mica sparks are produced which sometimes start out to the distance of 0·1 inch. (Heinrich.) If two pieces of cloth joined together by a solution of caoutchouc in coal-tar be suddenly pulled asunder, or if any cotton fabric be quickly torn, light will be emitted and will be visible in the dark. (*Ed. Phil. J.* 10, 185.) (No light is developed by the breaking of ropes, silk strings, or wires, or by the splitting of wood.) Cylinders of the following substances, mostly crystalline, emit light when broken, provided the fracture be not clean, but small pieces are thrown off or cracks produced: Fluor-spar, rock-salt, sulphate of potash, rock-crystal, rose quartz, hyalite, topaz, cyanite, adularia, labrador, glassy tremolite, zeolite, yellow blende and sugar, especially Canary sugar and sugar-candy; these substances emit a much brighter light when pounded in a mortar. Bitartrate of potash, Rochelle salt, and glass tubes give out an indistinct light when broken; alum, borax, and Glauber's salt emit none on being broken, but all these substances give out light when pounded in a mortar. (Heinrich.) Tartaric acid becomes luminous when pounded (Morion's *J. Chim. Med.* 3, 287); so likewise do large masses of beef and mutton suet when bruised by beating. (Bauernfeind, *Kestn. Arch.* 18, 370.)

Phosphorescence produced by rubbing.—The following substances emit light when rubbed together: Diamonds which become phosphorescent by insolation or heating, chlorate of potash, heavy spar, strontianite, burnt lime, Canton's phosphorus, fluor-spar, many kinds of statuary marble, dolomite, arragonite, anhydrite, Homberg's phosphorus, phosphorite from Estremadura, glass, porcelain, all precious stones and vitreous minerals (the brightest light is emitted by milk quartz and adularia, the faintest by jasper), blende, calomel (*comp.* Castillo, *J. Pharm.* 13, 158), corrosive sublimate, sulphate and phosphate of mercury, loaf-sugar, sugar-candy, and resins. (Dessaignes.)—Also: sal-ammoniac, nitre, alum, and blue vitriol (this last only after drying, the pieces being rubbed together while yet warm), borax, rock salt, witherite, double refracting spar, calcspar, many granular limestones, many kinds of alabaster, fluor-spar, apatite, pharmacolite, rock-crystal, quartz, amethyst, agate, chalcedony, hornstone, red and band-jasper, opal, corundum, topaz, adularia, common felspar, labrador, lapis lazuli, tourmalin, pyrope, wetz-schiefer, elastic stone, baked earthenware, calamine, iron pyrites (the last shines by combustion), tinstone, magnetic iron ore, and blood-stone. (Heinrich.) Phosphorescence is likewise exhibited by wet crystals of nitrate of baryta (not by dry ones) when violently thrown one against the other (A. Werner, *J. pr. Chem.* 14, 249); manna-sugar, and the so-called subresins. (Bonastre, *J. Pharm.* 10, 191.) According to Mills (*Ann. Phil.* 23, 235), acetate of lime evaporated to dryness and heated to 120° C. also emits light when rubbed with a spatula.

No phosphorescence of this kind is exhibited by any of the metals, or by any metallic sulphurets except blende; the hydrates of potash and soda,

all salts of ammonia, potash, and soda, except chlorate of potash; gypsum; the heavy metallic oxides; minerals containing heavy metallic oxides in large quantity; all heavy metallic salts except the mercurial salts above mentioned; all vegetable substances except sugar, resin, and certain liquids; all animal substances. (Dessaignes.) Moreover: sulphur, the Bolognian phosphorus, cyanite, steatite, lime, meerschaum, asbestus, teeth, bones, antlers, horns, and amber. (Heinrich.)

As a general rule, the same bodies emit light when rubbed with rock-crystal, an etching needle, or a revolving-grindstone; on the latter, phosphorescence is also exhibited by serpentine, zeolite, realgar, sparry iron ore, galena, and Rochelle salt: the friction-light which is generally of a pale yellow colour, is, when produced by the grindstone, of a fiery red. When large grindstones are used, the rise of temperature is inconsiderable (?), for the pieces of fluor-spar which fly off soon cease to shine. (Heinrich.)

Diamonds which do not become luminous by ordinary rubbing emit light when strongly rubbed one against the other, by which small fissures are produced within them. (Dessaignes.)

A peculiar smell is produced when many substances, luminous as well as non-luminous, are rubbed together: on rubbing together pieces of quartz in the air, a black powder is produced, and a white one if they are rubbed under water. (Dessaignes.)

The emission of light also takes place in vacuo, and under water, provided the latter does not exert a solvent action.

The light is white, yellow, red, or blue, according to the nature of the bodies: its duration is in most cases merely momentary; the diamond, however, shines for a minute when rubbed, and adularia continues luminous for some time and through its whole mass, when flaws have been produced in it by pressure. (Dessaignes.) The intensity of the light in any particular substance is greater, the more it has been previously heated, —provided the heat has not been raised to redness, in which case the body exhibits no more phosphorescence. A body cooled to a very low temperature, exhibits little or no phosphorescence when pressed. (Dessaignes.)

The following substances become luminous when rubbed with an ordinary quill-feather: Apatite, fluor-spar, rock-crystal, quartz, agate, chalcedony, lapis-lazuli (these five only when newly fractured), siliceous slate, felspar, mica, tremolite, the so-called crystalline sandstone and other varieties, lithomarge and white clay (Heinrich); Canton's and Homberg's phosphorus, dolomite, many kinds of blende, corrosive sublimate, and loaf-sugar (Dessaignes). The diamond alone shines when rubbed with wool or with a brush. (Dessaignes.)

Sulphate of cinchonin shines with a greenish light when rubbed in a basin at 100°; so likewise does sulphate of quinin, and with greater intensity; both substances become, at the same time, positively electrical. (Callaud, Stratingh.)

All precious stones (excepting diamond), marble, many kinds of blende, and loaf-sugar, become luminous when struck with a wooden or steel hammer. (Dessaignes.)

Phosphorescence from pressure on pulverized bodies.—The following substances in the state of powder emit light when struck on the anvil with a hammer, or pressed in the fire-syringe. Arragonite, calcspar, marble limestone, chalk, apatite, alabaster, fluor-spar, amethystine rock-crystal, chalcedony, felspar, mica, chlorit-schiefer, tremolite, and (very faintly) agalmatolite and steatite. These are in fact the bodies which

shine when heated, and the heat which the pressure produces is the cause of the luminosity. (Heinrich.)

When heavy spar, carbonate of baryta, carbonate of strontia, limestone, chalk, dolomite, Canton's and Homberg's phosphorus, and magnesia are heated either to redness or to whiteness and struck as soon as they have ceased to emit light, the luminosity reappears and continues for a longer time. This development of light is perhaps of a different kind. (Dessaignes.)

Liquids.

Water, aqueous solution of potash, acetic acid, alcohol, ether, volatile oils, and olive oil become luminous when rapidly compressed in a glass fire-syringe. (Dessaignes.) The same result is obtained with saline solutions. (Heinrich.) The light shows itself most strongly in that part of the liquid which is farthest from the piston, and quickly disappears. The experiment may be several times and uninterruptedly repeated with the same water, the temperature perhaps rising to 5° C. (Heinrich.)

Elastic Fluids.

Air, oxygen, and chlorine are, according to Saissy and Dessaignes, the only gases which emit light in the glass fire-syringe; according to Heinrich, this effect is also produced by hydrogen, nitrogen, nitrous oxide, and carbonic acid gas. (The assertion that hydrogen gives the brightest light and at the same time the greatest heat, excites a suspicion that the gas used in the experiments was mixed with common air.) The luminous appearance is produced with greater certainty when to the lower surface of the piston there is attached a sponge moistened with water,—or still better with solution of alum,—or else some fine threads of glass or asbestus,—on account of the action of the points (Schweigger, *Schw.* 40, 10). Spongy platinum attached to the piston does not favour the production of light. (Pfaff. *Schw.* 40, 1.) Thénard (*Ann. Chim. Phys.* 44, 181; also *Pogg.* 19, 442) attributes this light merely to the combustion of the leather of the piston and the grease used to lubricate it, in the compressed gases, inasmuch as this appearance has been observed only in air, oxygen, and chlorine. When the piston is made of brass covered with felt and lubricated with water, no light is seen, unless the felt has not been sufficiently moistened; neither is there any luminous appearance produced when the tube has been carefully cleaned from grease with caustic potash. Since the luminosity of gases shows itself only when the piston fits the tube very closely, and this close adaptation is not easily attained by the use of water,—and moreover, since some of the following experiments appear to confirm the fact of the development of light by the compression of gases,—the matter must for the present be looked upon as undecided. (Gm.)

Detonating bulbs (*i. e.* glass bulbs hermetically sealed and nearly empty of air) when thrown on the ground, exhibit a faint white light in bursting. (Helwig, *Gilb.* 51, 112.) — Vapour-bulbs (glass bulbs filled with alcohol, and burst by heating) give no light. (Heinrich.)

Airpump-light. A glass cylinder bound over with a strong bladder and exhausted of air appears, when the bladder breaks by the pressure of the external air, to be filled with a white light which is brighter in proportion as the cylinder was more completely exhausted of air. (Dessaignes, *Gilb.* 49, 310; Heinrich.) This light is undoubtedly caused by the

pressure exerted on the exceedingly rarefied air of the cylinder and the portion which first enters by that which rapidly follows it. Deparcieux observed light on the bursting of a glass bulb closed and full of air under an exhausted receiver.

Airgun-light. When an airgun is discharged, light is sometimes seen at the mouth of the barrel; according to Leyser (*Gilb.* 8, 340), only when the barrel is of iron, not when it is lined with brass. According to Heinrich, the gun must be fully charged, and even then only the first two or three discharges are accompanied by light, whether the gun be loaded with ball or not. The light is also apparent when the barrel is lined with lead, and most clearly when it is made of glass; it is not produced when the barrel is very wide, unless it be partly divided by a cleft ramrod. Leyser and more particularly Hart (*Qu. J. of Sc.* 15, 64), assert that light is not produced unless the barrel contains dust, or powdered fluor-spar or sugar is put into it; this would show that the light is produced by friction. According to Schweigger (*Schw.* 40, 22), the development of light is favoured by holding a crust of quartz-crystals or a coil of wire before the mouth of the barrel.

Light is seen in the sudden decomposition of peroxide of hydrogen, iodide of nitrogen, chloride of nitrogen, and oxide of chlorine; in these decompositions, gases are suddenly set free which probably produce light by pressing on the surrounding air or the undecomposed portion of the gaseous compound.

d. Luminous appearances accompanying Crystallization.

Many salts in crystallizing from their aqueous solutions, and benzoic acid in passing from the state of vapour into the crystalline condition, often exhibit a brilliant, sparkling light,—whilst in other instances, the same substances, under circumstances precisely similar, present no appearance of the kind. This phenomenon probably depends in every case on the passage of the body from the amorphous to the crystalline state, and is precisely analogous to the luminous appearance which accompanies the crystallization of arsenious acid (p. 105), and the phosphorescence of other amorphous bodies when heated (p. 106).

Pickel observed sparkling appearances in all parts of a vessel in which sulphate of potash was crystallizing; this continued for an hour. Schönwald saw sparks emitted during the evaporation and crystallization of a solution of 1 part of common salt and 2 parts of sulphate of potash, and found that the resulting crystals were luminous when rubbed.—Schiller dissolved in hot water a mixture of sulphate of potash, cream of tartar, and a small quantity of common salt which had been fused at a high temperature, and filtered the solution; during the crystallization flashes of light continued to dart through the liquid for several hours, and the crystals still shone when they were removed with a spatula several days after. According to Giobert, sulphate of potash does not emit light in crystallizing, when it contains sulphate of magnesia mixed with it; the light is first seen when the liquid becomes moderately concentrated and begins to crystallize by cooling; during slow evaporation no light is emitted. The larger the surface of the vessel, the brighter is the light; it seems also to be strengthened by previous exposure of the liquid to the sun. The crystals shine with the greatest brightness after the liquid has been poured off; but they cease to shine when dried upon blotting-paper.—Crystals which had separated from a solution of sulphate

of cobalt and potash at — 12° C. emitted sparks for half an hour after the liquid had been poured off. (Herrmann.)—A solution of several pounds of sulphate of potash crystallizing at + 20° C. emitted light for two hours; pieces of the crystalline crust even continued to shine when taken into the hand and their light grew stronger when they were rubbed. When a glass rod was moved over the crystalline crust at the bottom of the liquid, its track was marked by a luminous line. When the same saline mass was redissolved by heating the supernatant liquid and again crystallized by cooling, it was no longer phosphorescent. (Berzelius and Wöhler.) On evaporating a solution of bisulphate of potash in a porcelain basin, the crystals of neutral sulphate of potash which formed, emitted a strong light for half an hour and continued to shine even when taken out of the liquid; the latter also exhibited a sparkling light, especially when stirred. (Pleischl.)—A solution of acid sulphate of potash, neutralized with carbonate of potash, filtered, evaporated to the crystallizing point and divided among a number of wooden and stone-ware crystallizing vessels, exhibited towards evening on the surfaces of all the vessels a succession of sparks, the emission of which continued with a peculiar noise for several hours, but ceased when the liquid had become quite cold; the mother liquid exhibited no more light when further evaporated. (Sager, *Br. Arch.* 36, 274.)

Crystallized neutral sulphate of potash dissolved in water and brought to the crystallizing point by evaporation never emits light: neither does fused sulphate of potash similarly treated,—for in cooling from a state of fusion it acquires a crystalline structure. But sulphate of potash fused with sulphate of soda in the proportion of equal atoms (in the proportion of 11 parts : 9 parts) yields, on cooling, an amorphous, fissured, crumbling mass of vitreous fracture, a saturated solution of which in boiling water prepared immediately after cooling, then filtered hot and slowly cooled, emits light. The formation of every crystal is accompanied by a bright spark. For the first few hours, the crystals continue to shine when taken out of the liquid and rubbed, but not so strongly as during their formation. They have the form of sulphate of potash, but contain about one atom of dry sulphate of soda mixed with every 2 atoms of sulphate of potash. When redissolved in water, they emit no light on crystallizing. If the mass is dissolved in water not quite boiling, and the solution slowly evaporated to dryness, no light is emitted, and the two salts crystallize separately. If the melted mass is exposed to the air for 24 hours before it is dissolved in water, but few luminous crystals are seen; and if it has been left undissolved for several days, in which case it appears to become crystalline and separate into its two component salts, none at all. A fused mixture of 3 atoms of sulphate of potash and 2 atoms of sulphate of soda similarly treated yields less light. When crystallized sulphate of potash and crystallized sulphate of soda are boiled together in water, a very faint light is sometimes observed during the subsequent crystallization: a portion of amorphous double salt appears therefore to be produced by the boiling.—A surer method of producing light, and of considerable brilliancy, is to fuse together 2 parts of sulphate of potash with 1 part of common salt, and treat the fused mass as above. The crystals obtained are the above-mentioned compound of sulphate of potash and sulphate of soda, free from common salt. A strong light is also obtained by treating in a similar manner a mixture of 8 parts of sulphate of potash with 3 parts of dry carbonate of soda. (If the fused mass be

extracted with a mixture of alcohol and acetic acid in order to remove carbonate of potash, the double sulphate of potash and soda remains in the crystalline state, and therefore emits no light when dissolved and crystallized.) Chloride of potassium fused with sulphate of soda likewise exhibits the luminous appearance. A bright light is also emitted by neutral chromate of potash fused with sulphate of soda, whereby crystals are formed, consisting mainly of the double sulphate of potash and soda with only 3 per cent. of chromic acid: moreover, by 2 parts of bichromate of potash fused with 1 part of dry carbonate of soda,—in which case crystals are produced having the form of sulphate of potash and containing 3 atoms of chromate of potash combined with 1 atom of chromate of soda; and finally by a mixture of 1 atom of seleniate of potash with 1 atom of sulphate of soda, which produces crystals having also the form of sulphate of potash, and containing only 5 per cent. of selenic acid, together with potash, soda, and sulphuric acid. (H. Rose.)

A saturated solution of fluoride of sodium very slowly evaporated emitted a great number of bright sparks of a pale yellow colour, which proceeded sometimes from one sometimes from another part of the crystals as they formed, increased when the liquid was disturbed, and did not cease till it was completely evaporated. On repeating the experiment with the same salt and the same vessel, nothing further was seen (Berzelius).—Likewise observed by H. Rose. (*Pogg.* 52, 589.)

A solution of nitrate of strontia, which had been for a long time exposed to air and light, emitted many sparks when evaporated and crystallized in a stoneware vessel; these sparks showed themselves particularly when the crystals were touched with a glass rod or metallic wire, and also when the vessel was shaken. On redissolving and recrystallizing the salt, this appearance was not reproduced, though the mode of experimenting was varied in every possible way. (Pfaff.) Likewise observed by Stieben. (*Pharm. Central* Bl. 1836, 400.)

A solution of 8 parts of acetate of potash evaporated till it ceased to swell up, and fell to pieces, shone brightly, when left over the fire, as if it were red hot. (Büchner.) (Slow combustion?)

On subliming benzoic acid with $\frac{1}{8}$ of its weight of charcoal powder on a plate covered with a glass receiver and strongly heated, Büchner observed numberless sparks moving up and down as long as the sublimation continued.

Addendum to the remarks on the incandescence of bodies (p. 107): A body does not always increase in density by incandescence. Uranotantalite, which exhibits vivid incandescence, has a sp. gr. of 5·517 before incandescence and 5·485 after.—Incandescence takes place without perceptible development of heat: at all events, no rise of temperature can be perceived in the case of oxide of chromium, in which the incandescence is very bright. (The development of light observed in the crystallization of arsenious acid from its solution in hydrochloric acid is likewise unattended with disengagement of heat.) Whilst according to this, many bodies in passing from the amorphous to the crystalline state merely develop light, others on the contrary develop heat, *e. g.* grape-sugar (p. 106). H. Rose, *Pogg.* 52, 589.)

CHAPTER 2.

HEAT.

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Synonymes. *Caloric, Chaleur, Wärmestoff, Wärmematerie.*

Heat or Caloric is that substance whose entrance into our bodies is supposed to occasion the sensation of warmth or heat, and its egress the sensation of cold.

Physical Properties.

1. It is invisible.

2. Without weight.—Oil of vitriol and water have the same weight before mixture and cooling as afterwards. The weighing of cold and heated balls in the air proves nothing.

3. It is very elastic, and shows great tendency to expand.—Two easily moveable bodies, heated in vacuo, repel one another,—a proof that heat is in its own nature repulsive. (Fresnel, *Ann. Chim. Phys.* 29, 57, and 107; also *Pogg.* 4, 355.)—The coloured rings formed between a lens and a flat plate of glass vary in tint when heated, in such a manner as to show an increase of distance between the lens and plate. (Baden Powell.)—The fine soft powder of silica separated by acids from solutions of that substance, or magnesia in a similar condition heated to redness in a platinum dish over a spirit lamp, appears to swim in the dish, becomes very mobile, and places itself horizontally when the dish is turned on one side—an effect which proceeds from the repulsive force of heat (or from the escape of heated air.* Gm.?) (Addams, *Phil. Mag. J.* 18, 415.)

4. Through a vacuum, through elastic fluids, and through many liquid and solid bodies, it spreads itself out from its origin in straight lines, as *Radiant Heat*, with a great and hitherto unmeasured velocity. Its in-

* This semifluid state of a pulverulent substance is well seen when bicarbonate of soda is heated in a large crucible for the purpose of converting it into carbonate; also in the conversion of oxalate of cerium into the peroxide of that metal by ignition. In these cases the effect is evidently due to the escape of heated gases: the fine particles of the powder *float* in the atmosphere formed around them by the gases before they finally escape. [W.]

tensity varies inversely as the square of the distance from the radiant point.—Rays of heat may, like rays of light, be concentrated by metallic mirrors, but not by glass mirrors or lenses, by which they are almost wholly absorbed. If two concave metallic mirrors be placed opposite one another at a distance of 77 feet, and a hot body placed in the focus of one of them, a thermometer in the focus of the other rises immediately; tinder is also set on fire. Ice placed in the focus of one of the mirrors produces instant cooling in the focus of the other; a thermometer suspended midway between the two mirrors is not sensibly affected. (Pictet, *Gilb.* 13, 120.)

A body placed in vacuo or in the air, and differing in temperature from the surrounding medium, radiates its excess of heat or absorbs the quantity in which it is deficient, with various degrees of facility according to the nature of its surface; it has therefore a specific *Radiating* and *Absorbing power*, to which are opposed the *Retaining* and *Reflecting powers*, —so that the latter increase in the same ratio as the former diminish, and conversely. If the radiating power of a surface covered with lamp-black be assumed = 100, that of a surface covered with resin will be 96, with sealing-wax 95, with crown-glass 90, with Indian ink 88, with ice 85, with isinglass and red lead 80, with graphite 75, with polished lead 19, with polished iron 15, with polished tin, copper, and gold 12. (Leslie.) —Black wool has greater radiating and absorbing power than green; then follows red, then yellow, then white. (Stark, *N. Edinb. Phil. J.* 17, 75); on the contrary: (Baden Powell, *ib.* 17, 228.)—Roughness of surface does not increase or diminish the radiating and absorbing power; in the case of rolled or hammered metals, it is increased by scratching the surface, because the denser surface is thereby removed; but with cast plates it is diminished by the same treatment, because the pressure caused by scratching increases the density in particular places. (Melloni.)

It is commonly supposed that a body placed in the air or in an empty space is constantly radiating a portion of its heat, whatever may be the temperature of the surrounding bodies; but since these bodies radiate heat in the same manner, the first-mentioned body receives heat from them at the same time that it gives out heat to them. If the surrounding bodies have the same temperature with the first, the quantities of heat emitted and absorbed will be equal, and the temperature of the first body will remain the same; if the surrounding bodies are colder, it will radiate more than it receives and will cool down; if they are hotter, its temperature will rise.—It is, however, superfluous to suppose such an interchange of heat to take place. For when two bodies separated by air or an empty space are equally hot, the elasticity of the heat is the same in both, each will hold the other in check, and the heat in both bodies will remain at perfect rest: when, on the contrary, one body is colder than the other, the tension of the heat in the former will be less than in the latter; and in consequence of this difference of tension, a quantity of heat will radiate from the hotter to the colder body until the equilibrium is established.

Difference of refrangibility exists among calorific as well as among luminous rays; the hotter the source of heat (*e. g.* the sun, an Argand lamp, white-hot platinum), the greater is the number of the more refrangible rays emitted from it; the lower the temperature of the source (*e. g.* metal heated but not to redness, vessels filled with boiling water), the greater is the number of the less refrangible rays which it emits. Every source of heat, however, sends forth a mixture of calorific rays of the most various

degrees of refrangibility, the proportion only varying according to the nature of the source. For these different rays of heat bodies exhibit different absorbing powers. Snow, whose whiteness shows that it reflects the variously refrangible rays of light in equal proportion, absorbs chiefly the less refrangible rays of heat and reflects the more refrangible. Hence it does not melt so quickly in direct sunshine as in the neighbourhood of stems of trees and other solid bodies, which, when warmed by the sun's rays emit calorific rays of less refrangibility,—not so quickly when freely exposed to an Argand lamp, as under a covering of black paper which does not touch the snow; not so quickly by the rays of an Argand lamp as by those from a piece of metal heated to 400°, when both are placed at such a distance that their heating powers are equal, &c. (Melloni.) This seems to show that the more refrangible rays of heat, when they are absorbed by bodies and afterwards emitted from them, are converted into rays of less refrangibility. Lamp-black, on the other hand, appears chiefly to absorb the more refrangible rays.

A body cools in vacuo the more quickly: 1. the greater the radiating power of its surface; 2. the greater the extent of its surface; 3. the smaller its mass; 4. the less its specific heat; 5. the higher the absolute temperatures of the body and the surrounding bodies and medium, with equal difference of temperature (thus a thermometer heated to 100° cools less quickly in an empty space at the temperature of 0° than it would if heated to 180° and placed in an empty space of the temperature of 80°). —Dulong and Petit.

Dufay, Maycock, and Prevost discovered, some years ago, that of the rays of heat which fall upon a thin plate of glass a small portion are transmitted; Delaroche also showed that the number of rays transmitted increases as the temperature of the source of heat approaches to that of ignition, and that rays which have passed through one plate of glass suffer much less diminution by transmission through a second; Brande likewise saw (*Ann. Chim. Phys.* 19, 201) a thermometer placed in the focus of a plano-convex lens held towards the flame of burning olefiant gas rise about 2 5° C., whilst the lens was not sensibly heated. To these observations have since been added the following important discoveries of Melloni, who, in his experiments made use of the thermo-multiplier, an instrument depending upon thermo-electric action and highly sensible even to the smallest variations of temperature. All transparent substances, even those which are so dark-coloured as to appear almost opaque, like black glass, crude pyroligneous acid, and balsam of Peru, allow rays of heat to pass through them, though in different quantities and of different qualities: with reference to this property such bodies are said to be *diathermanous*. Common salt transmits all rays of heat equally well; most diathermanous bodies chiefly transmit the more refrangible and absorb the less refrangible rays (common salt covered with lamp-black is the only substance chiefly pervious to the less refrangible rays). Of 100 rays of heat proceeding from an Argand lamp and falling on plates of the following substances, 0·002 mètre in thickness, the quantities transmitted are as follows: Transparent rock-salt 92·3, flint-glass 67, sulphuret of carbon and proto-chloride of sulphur 63, double refracting spar and rock crystal 62, smoky topaz 57, Brazilian topaz 54, transparent lead-spar 52, crown-glass 49, white chalcedony 35, translucent heavy spar 33, oil of turpentine 31, fat oil 30, transparent aqua-marine 29, translucent borax 28, green Brazilian tourmalin 27, brown balsam of

copaiba 26, translucent adularia 24, ether 21, transparent gypsum 20, oil of vitriol 17, nitric acid, alcohol and citric acid 15, transparent alum 12, water 11. The non-transmitted portion of the calorific rays is partly reflected, partly absorbed. With rock-salt reflection alone takes place; for a plate of this substance, 0·048 mètre thick, transmits as many rays as one which is 0·002 mètre in thickness,—whilst two thin plates of rock-salt laid one upon the other transmit less light on account of the double reflection. Hence, of 100 rays of heat falling perpendicularly upon rock-salt, 92·3 are transmitted and 7·7 reflected: when the incidence is oblique, the quantity reflected is somewhat greater. With other diathermanous bodies also the quantity of heat reflected amounts to 7·7 per cent. (athermanous bodies reflect a great deal more, *e. g.*, brass 11·3 times as much). But these diathermanous bodies likewise absorb various quantities of the less refrangible heat-rays which fall upon them, the quantity absorbed being increasing with the thickness of their mass. Double refracting spar 0·002 met. thick transmits 62 per cent. of heat, and at the thickness of 0·092m. only 53 p. c.; plate-glass of the thickness of 0·002m. transmits 61·9 p. c.; of 0·004m. 57·6, and of 0·008m. 55·8 p. c.—By means of a lens of rock-salt, rays of heat may be brought to a focus,—or if they proceed from the focus they may be refracted in parallel lines just as well as rays of light by a glass lens: the focal distance for heat however is somewhat greater than that for light, because the calorific rays are less strongly refracted. Rock-salt transmits rays of heat of all degrees of refrangibility, just as white glass transmits all the luminous rays. But most other diathermanous bodies give passage chiefly to the more refrangible rays of heat, as violet glass transmits the more refrangible rays of light. Rock-salt blackened with lamp-black, which transmits in preference the less refrangible rays, is to a certain extent analogous to red glass in relation to light. Glass coloured bluish green with oxide of copper appears likewise to absorb the more refrangible rays of heat. When the light of the sun is made to pass, first through water which absorbs the less refrangible, then through glass coloured with oxide of copper which takes up the more refrangible rays of heat, it is totally deprived of its heating power. (Melloni.)

When the light of the sun is transmitted through a prism of crown-glass which throws the maximum of heat into the red, and the dark part of the heat-spectrum situated beyond the red is divided into six zones, the outermost of which shows the same temperature as the violet, the next the same as the indigo, &c, it is found on interposing a film of water, 0·001 metre in thickness (or a plate of gypsum or alum,—glass acts less strongly), between the prism and the spectrum, that the heating power diminishes more and more as the distance from the violet increases.

	Violet.	Indigo.	Blue.	Green.	Yellow.	Orange.	Red.	Zone. 1	2	3	4	5	6
Without the film of water	2°	5°	9°	12°	25°	29°	32°	29°	25°	12°	9°	5°	2°
With the film of water ..	2	4·5	8	10	20	21	20	14	9	3	1	0·5	0

Water in fact absorbs the calorific rays the more completely, the less refrangible they are, whilst it transmits completely the most refrangible rays at the violet extremity. When the film of water is 0·3 metre thick, the maximum of heat is found at the commencement of the green, and the heat

spectrum extends but a little way beyond the red into the dark space.—This explains Seebeck's discovery (page 165), viz. that the maximum of heat is found in different parts of the spectrum according to the nature of the prism. The smaller the number of calorific rays which any substance transmits (p. 215), whilst it retains the less refrangible rays, the more nearly does the maximum of heat in the spectrum formed by a prism made of that substance approach to the violet; whence, according to Seebeck, a prism of water places it in the yellow, of oil of vitriol in the orange, of crown-glass in the red, of flint-glass beyond the red; and with a prism of rock salt, which completely transmits even the least refrangible rays, the maximum of heat is situated, according to Melloni, in the dark space, and as far removed from the red as the red itself is from the violet. With some glass prisms, the maximum of heat approaches more nearly to the violet, in proportion as the ray of solar light passes through a thicker part of the prism,—because, in this longer passage through the glass, a greater number of the less refrangible heat-rays are retained. (Melloni.)

If light and heat are regarded as identical in substance, it may be supposed that the rays of heat approach more nearly to those of light in proportion as their motion is more rapid (which also implies increased refrangibility). The hotter the source of heat, the greater is the number of the more rapidly moving calorific rays emitted from it; and these pass without sensible absorption through glass and other diathermanous bodies, and then also through several, whilst the more slowly moving heat-rays are absorbed. (Ritchie.)

¶ The subject of *Radiant Heat* has lately been further investigated by Knoblauch. (*Pogg.* 70, 205 and 337; 71, 1: abstr. *Ann. Chem. Pharm.* 74, 193.) The principal results obtained by this philosopher are as follows.

1. *The quantity of radiant heat transmitted through diathermanous bodies is not* (as former experiments seemed to show) *directly proportional to the temperature of the source, but depends only on the constitution of the diathermanous body,—each body being permeated by certain calorific rays more readily than by others, whether those rays are emitted at a higher or at a lower temperature.*—Thus when rays of heat from incandescent platinum, the flame of alcohol, of an argand lamp, and of hydrogen gas, were made to pass through colourless glass and alum, and then to fall on a thermo-multiplier, the distance of which was so adjusted as always to give a deflection of 20° by direct radiation when the diathermanous bodies were removed,—the following results were obtained:

Sources of Heat.	Direct Radiation.	Colourless glass $1{\cdot}3^{mm}$ thick.	Alum $1{\cdot}4^{mm}$ thick.
Incandescent platinum	20°	12°	8·25°
Flame of alcohol.....	20	11	7·50
Argand lamp	20	15	10·50
Hydrogen gas	20	12	7·75

Through rhombohedral talc-mica (*Kali-und magnesia-glimmer*), the heat from the flame of hydrogen passes less easily than that from either of the other three sources.—By experiments made with a cubical vessel containing hot water, also with a cylinder of untinned iron heated over an

Argand lamp, and a spiral of platinum wire heated to various degrees of incandescence, it was likewise found that when the heat emitted from one and the same body at various temperatures is made to pass through different diathermanous bodies, the quantity of heat transmitted is not proportional to the temperature of the source, but depends upon the nature of the diathermanous media.

2. With regard to the heating of bodies by radiation, Knoblauch shows that: *The heating effect produced, when the radiated heat which reaches the bodies is of given intensity, is totally independent of the temperature of the source, and determined only by the nature of the absorbing bodies, which receive certain rays more readily than others.*—Thus when the heat from an Argand lamp and a metal cylinder heated to 80° R. was made to fall on a plate of metal covered with lamp-black on the side turned towards the thermo-pile, but having its other side covered, in one case with carmine, in the other with black paper, the following results were obtained:

Sources of Heat.	Direct Radiation.	Interposed	
		Carmine.	Black Paper.
Argand lamp	35°	9·50°	10·75°
,, ...	50	13·75	15·25
Cylinder heated to 80° R.	35	10·87	10·12
,, ,, ...	50	15·62	14·00

To determine the manner in which the heating of bodies by radiation is affected by their thickness, experiments were made with a metallic plate covered with layers of varnish, &c., of various thicknesses. The following table exhibits the results.

Sources of Heat.	Direct Radiation.	Metallic Plate.									
		Naked.	Covered with								
			Layers of Varnish.				Layers of Black Lac.				Laye White
			1	2	4	8	thin	thick	thicker	thickest	thin
Argand lamp ..	35°	6·50	8·25	8·25	8·25	8·25	7·12	8·25	8·62	9·5	7·25
,, ..	60	10·50	14·50	15·12	15·62	15·75	14·50	16·25	17·37	18·12	16·12
Cylinder heated to 80° R....	35	6.50	9·00	9·25	9·50	9·50	9·12	9·87	11·62	12·00	8·75
	60	10·50	17·50	18·12	20·12	20·75	18·62	20·25	21·37	22·12	17·00

Hence it follows, that within the limits of these experiments, *the substances employed are more strongly heated, in proportion as their thickness is greater.* Precisely the contrary result was obtained by Leslie and Melloni. The discrepancy is explained as follows. The amount of heat imparted to a body by radiation increases in proportion to the number of absorbing layers to which the heat can penetrate. But the heating effect attains its maximum at a certain thickness, beyond which the heat imparted by radiation cannot attain. Now in Knoblauch's experiments, the thickness was never too great to allow each successive layer to be

heated, and thus to act upon the metallic surface. In the observations of Leslie and Melloni, on the contrary, the interposed diathermanous plates were so thick, that only a small portion of the heat absorbed penetrated to the side which was turned towards the thermoscope.

3. With respect to the *radiating powers* of different substances at the same temperature, Knoblauch confirms the law laid down by Melloni, viz. that *the radiating power of a body is influenced by scratching its surface, only in so far as its density and hardness are thereby altered*:—also the result previously obtained by both Rumford and Melloni, that: *the radiating power increases with the thickness of the radiating film*,—a law which furnishes another proof of the correspondence between radiation and absorption. Knoblauch likewise observes that the equality of the radiating and absorbing powers is absolutely true as regards one and the same body; but that with respect to different bodies, it cannot be maintained that a body which at a certain temperature exhibits a higher radiating power than another, necessarily also possesses a greater absorbing power;—for the proportion between the quantities of heat absorbed by two bodies varies with the nature of the calorific rays.—Lastly, it is shown that the radiating power of a body is the same, however different may be the calorific rays by which it is heated.

4. *The heat radiated from the most various solid bodies, such as metal, wood, porcelain, leather, cloth, pasteboard, &c.—of different thicknesses and different conditions of surface appears, when tested by all the means at our command, to be of the same nature, in whatever manner it may have been excited.*—In the experiments by which this result was obtained, the temperatures of the sources of heat varied from 25° to 90° R.—This result is of some interest with reference to the determination of specific heat; for if the ice in the calorimeter were to absorb the heat radiated from different substances in different degrees, the quantity of ice melted would not be a direct measure of the quantity of heat.

5. *Alteration of heat by Irregular Reflection.* Melloni has remarked that a white surface reflects, with various degrees of intensity, the heat of a Locatelli's lamp, according as it is used with or without the glass chimney,—also the heat of incandescent platinum, and that of a metal cylinder heated to 400° C.—Metallic plates with rough surfaces are the only bodies which reflect equally the heat from all sources,—whilst lamp-black gives a scarcely perceptible dispersion with any.—The following table contains the results of a number of experiments in relation to this subject. The source of heat used was an Argand lamp, and the heat, after reflexion from the various substances mentioned at the head of the table, was made to traverse the several diathermanous media mentioned in the first column,—the object being to determine whether the calorific rays, after diffuse reflection from those various surfaces, would pass through the different media in equal or unequal quantities.

Substances interposed.	Direct radiation.	Deflection after interposition (without reflection).	Deflection after interposition and reflection from :—																
			Gypsum	Chalk.	White lead.	Peroxide of tin.	White oil-colour.	Porcelain.	White satin or taffetas.	White velvet.	White linen.	White paper.	White cotton.	White wool.	Mother of pearl.	Ivory.	Silver.
Red glass	13°	7·63	9·00	9·00	9·00	9·21	9·04	9·09	9·04	9·04	9·21	9·29	9·21	9·00	8·33	7·37	7·58
Blue glass		5·79	6·58	6·50	6·54	6·46	6·21	6·58	6·50	6·13	6·46	6·46	6·50	6·46	6·13	5·96	5·83
Alum		4·38	5·71	5·75	5·71	5·71	5·54	5·67	5·46	6·67	5·71	5·75	5·83	6·58	6·13	5·83	4·38
Rock-salt	25°	22·25	23·06	23·06	23·13	23·00	23·00	22·94	23·13	23·00	22·56	22·56	23·13	23·13	22·56	21·94	22·25
Calcspar		14·94	20·19	20·25	20·25	18·38	20·19	20·31	19·50	21·31	20·31	20·25	20·44	20·81	19·06	17·44	14·86
Gypsum		11·75	16·87	16·85	16·75	15·12	16·88	16·81	16·81	18·69	16·88	16·88	16·94	18·31	17·56	15·81	11·59

Substances interposed.	Direct radiation.	Deflection after interposition (without reflection).	Deflection after interposition and reflection from :—											Deflection after interposition and reflection from :—	
			Oxide of copper.	Tannate of peroxide of iron.	Asphalt-lac.	Black satin or taffetas.	Black velvet.	Black paper.	Black cloth.	Black morocco.	Black glass.	Unlinned iron-plate.	Deflection after interposition (without reflection.)	Charcoal.	Brown coal.
Red glass	13°	9·32	9·96	10·14	10·64	9·61	8·79	8·03	9·32	9·50	8·25	9·29	9·06	8·25	10·25
Blue glass		7·66	7·86	7·89	8·18	8·07	7·25	6·96	7·75	7·43	6·79	7·11	7·88	7·50	7·56
Alum		5·85	6·29	6·64	6·57	6·79	6·11	5·36	7·07	6·71	5·94	5·57	5·75	5·31	6·06
Rock-salt	25°	22·25	23·12	22·69	22·88	22·94	21·50	21·12	22·12	22·75	20·88	22·12	22·12	21·31	22·12
Calcspar		16·75	20·06	20·94	20·38	19·81	18·62	14·75	20·00	20·06	15·12	16·81	16·50	14·69	19·50
Gypsum		14·00	16·00	16·88	16·12	16·19	15·31	12·77	17·25	16·69	12·62	13·69	14·44	13·12	16·56

The rays of heat reflected from certain homogeneous bodies passed in unaltered proportion through the diathermanous media. Such was the case with birchwood, cork, and mahogany; also with the simple metals and metallic alloys.

Heat is therefore altered by diffuse reflection in very different ways; in a high degree by some bodies, not at all by others. These alterations, in the case of unpolished bodies, are independent of their degree of roughness:—in the case of metallic surfaces, it is even indifferent whether they are used in a state of high specular polish or in any other condition of surface.

By making use of incandescent platinum, the flame of alcohol, and a heated metal cylinder as sources of heat, it was found that: *The changes produced in heat by irregular reflection are affected by the nature of the source of heat as well as by the nature of the reflecting surface.* And in particular, that the modifications, which are very considerable in the rays of the Argand lamp, are less in those of red-hot platinum, still less in those of the alcohol flame, and in the case of the metal cylinder heated to any temperature between 20° and 90° R, they become absolutely nothing.

It is easily seen how by these modifications the rays of heat reflected from different substances, may to a certain extent, alter their relations one to another. Thus, the heat of an Argand lamp when reflected from carmine, passes through gypsum with less facility than when reflected from white velvet. The rays of incandescent platinum pass equally well through gypsum after reflection from those surfaces; and the heat of an alcohol flame passes through that medium after reflection from carmine better than after diffuse reflection from white velvet.

On repeating the experiments with the four above-mentioned sources of heat with reference to a different object, it was found that surfaces which affect *equally* the rays from any one source of heat, *e. g.* of an Argand lamp, likewise modify in an equal degree the rays from any other source. The following lists contain those substances which scatter the rays of heat in such a manner that, as far as regards their passage through red glass, blue glass, alum, rock-salt, calcspar, and gypsum, they are not to be distinguished one from the other. The bodies in (1) have likewise this peculiarity,—that the heat irregularly reflected at their surfaces is undistinguishable from non-reflected heat.

(1.) Gold, silver, platinum, mercury, iron, tin, zinc, copper, lead, alloy of lead and tin, brass, German silver, untinned iron plate. (2.) Gypsum, chalk, white lead, white oil-colour, porcelain, linen, white paper, blue paper, white cotton, grey calico, Paris green, green cinnabar, chrome yellow, black lac. (3.) Birch-wood, cork, mahogany, yellow marble. (4.) White satin, black satin, white taffetas, black taffetas. (5.) Blue velvet, black velvet. (6.) Yellow leather, brown morocco. (7.) Light cloth, black cloth. (8.) Blue flock-paper, green flock-paper. (9.) White wool, red wool. (10.) Cinnabar, oxide of copper.

Of the following substances, those contained in the same division exhibit a similar but not exactly equal action.

(11.) Carmine, madder, red flock-paper. (12.) White velvet, white wool, green flock-paper. (13.) White lead, Diessbach blue. (14.) Black velvet, green oil-cloth. (15.) Black paper, black glass. (16.) Coal, coke, plumbago. (17.) Lamp-black, animal charcoal.

The following substances, with reference to the dispersion of heat, cannot be included in either of the preceding groups.

(18.) Ultramarine. (19.) Peroxide of tin. (20.) Tannate of per-

oxide of iron. (21.) Indian ink. (22.) Red taffetas. (23.) Green taffetas. (24.) Dark red velvet. (25.) Light red velvet. (26.) Green velvet. (27.) Black morocco. (28.) Brown Manchester. (29.) Mother of pearl. (30.) Ivory. (31.) Charcoal. (32.) Brown coal.

It is also shown that: *The changes which heat undergoes by diffuse reflection are wholly due to an elective absorbing power of the reflecting surface for certain of the calorific rays which are sent to it.* In this respect, the phenomena are perfectly analogous to those which are observed in the diffuse reflection of luminous rays.

With the exception of the metals, which reflect all calorific rays equally well, and of charcoal which absorbs them all, it cannot be said of any substance yet examined, that it reflects heat better or worse upon the whole than another; inasmuch as the proportion varies with each radiation.

6. The preceding results show, with regard to the sources of heat employed, that the diversity of quality in the emitted rays is greatest in the Argand lamp, less in the incandescent platinum, and still less in the alcohol flame,—while in the case of the cylinder heated to 80° R. it vanishes altogether. Generally, the heat emitted from the most various solid bodies between the temperatures of 50° and 90° R (144·5° and 234·5° Fah.) is perfectly *homogeneous* or *monochromatic.*

The variety of *calorific tints* in the heat of incandescent platinum increases with its temperature. It is not however universally true that, of two sources of heat, that which has the higher temperature has also the greater variety of calorific rays; *e. g.* red-hot platinum emits rays of greater diversity than those emitted by the flame of alcohol.

It is likewise remarkable that the variety of calorific rays emitted from different sources is greater or less, just as those sources contain a greater or less variety of the coloured rays of light: thus, it is evident that the flame of the Argand lamp is richer in this respect than red-hot platinum, and the platinum richer than the alcohol flame. ¶

The calorific rays of a body heated to dull redness may be polarized like rays of light (p. 164), so that they will or will not be reflected from a second surface and afterwards affect a thermometer, according to the position in which that surface is placed. (Bénard, *Gilb.* 46, 384.)—Rays of heat may be polarized by transmission through tourmalin or mica, depolarized by doubly refracting crystals, &c. (Forbes, Melloni.)—Baden Powell denies the polarization of heat.

According to Pouillet's approximate estimation, the temperature of the sun is between 1461° and 1761° C, and it sends annually to the earth as much heat as would melt a stratum of ice surrounding the whole earth and 31 mètres in thickness. The temperature of space, according to the same calculation, is about — 142° C; but this likewise imparts yearly to the earth a quantity of heat sufficient to melt a similar stratum of ice of the thickness of 26 mètres.

When heat is restrained in its radiating motion by the adhesive force of liquid and solid bodies it diffuses itself within them slowly and with a creeping motion; it is *conducted* by them.—According to Fourier's hypothesis, the conduction of heat consists in radiation from one atom to another.

Conducting power of solids. The metals are the best conductors of heat. If the conducting power of gold be assumed = 1000, that of platinum is 981, of silver 973, copper 898, iron 374, zinc 363, tin 304,

lead 180, marble 24, porcelain 12, tiles 11·4. (Despretz.) If a number of metallic rods of equal length, breadth, and weight, and covered with wax, be equally heated at one end, the wax on the copper will be melted for a distance of 3·5 inches, on the silver 2·5, and on the platinum and palladium 1 inch. (Wollaston.) *Comp.* N. W. Fischer (*Kastn. Arch.* 14, 147; *Pogg.* 19, 507; 52, 632.)—The passage of heat from one solid body to another in close contact with it causes retardation. (Despretz.)—N. W. Fischer's assertion (*Pogg.* 19, 513) that when water is placed in contact with the heated end of a metallic bar, the heat moves on to the cold end, has been to a certain extent confirmed by Mousson (*Bibl. univ.* N. S. 12, 418) but contradicted by Schröder (*Pogg.* 46, 135) and Böttger (*Pogg.* 50, 60).—Porous bodies are remarkably bad conductors, *e. g.* those of organic structure, such as wood, wool, feathers, &c.

¶ Senarmont (*N. Ann. Chim. Phys.* 21, 457) has investigated the conduction of heat in crystallized bodies. The mode of experimenting was to heat a cylindrical plate of the crystal in the direction of its axis, and trace the form of the isothermal curves on the two faces by means of melted wax. A small tube of platinum was inserted through the centre of the plate in the direction of its axis, bent at right angles at the lower extremity and heated by a lamp,—a current of air being at the same time sent through the tube by means of an aspirator. The two bases of the cylinder were covered with wax, which, being melted by the heat, traced out on the surface a curve line whose form was determined by the conducting power of the crystal in different directions.

Plates of homogeneous substances, such as glass and zinc, treated in this manner, gave circles, the centre of which was at the source of heat.

On a plate of calcspar cut perpendicular to the axis of symmetry, the curves were circles with their centres in the axis. On plates parallel to the direction of natural cleavage, the curves were also circles, exhibiting a slight tendency to elongate in the direction of the principal section. On plates parallel to the axis of symmetry, and having their plane perpendicular to one of the faces of the primitive rhombohedron, the curves were ellipses very regular and well defined, and having their longer axes in the direction of the axis of symmetry. The ratio of the axes was 1·118. These experiments show that the axis of symmetry is a direction of greater conductibility.—Similar results were obtained with quartz, the ratio of the axes being 1·31.—It may therefore be inferred that: *In media constituted like crystals of the rhombohedral system, the conducting power varies in such a manner, that, supposing a centre of heat to exist within them, and the medium to be indefinitely extended in all directions, the isothermal surfaces are concentric ellipsoids of revolution round the axis of symmetry, or at least surfaces differing but little therefrom.*

On plates of gypsum perpendicular to the crystallographic axis, the curves were ellipses, the ratio of the axes being 1·23. The author was unable to experiment upon plates perpendicular to the direction of easiest cleavage; but there is every probability that the curves in this case would also be elliptical. It may therefore be inferred that: *In media constituted like crystals with two optic axes, if we suppose a centre of heat to exist within, and the crystal to be indefinitely extended in all directions, the isothermal surfaces will be ellipsoids with three unequal axes, or curve surfaces differing but little therefrom.* It is probable also that the principal axes of these isothermal surfaces coincide with the crystallographic axes, when the latter are likewise axes of symmetry.

No experiments were made with crystals belonging to the regular system, on account of the difficulty of procuring suitable specimens. It is probable, however, that in media of this nature, the isothermal surfaces would be spherical. ¶

Conducting Power of Liquids. When heat is communicated to the bottom of a liquid, it diffuses itself quickly and uniformly throughout; not, however, by conduction, *i. e.* by radiation from particle to particle, but in consequence of currents in the liquid itself,—the lower portion, which is heated and thereby expanded, ascending, while the colder and heavier portion sinks. The communication of heat from the upper to the lower part of a liquid takes place so slowly, that Rumford absolutely denied the existence of conducting power in bodies of this class; it has, however, been shown to exist in them by Thomson, Murray, and Dalton (*Gilb.* 14, 129, 158, and 184*); and, according to Despretz, the conduction of heat in liquids takes place according to the same law as in solids. —Respecting the supposed slower cooling of warm mineral waters, *vid.* Longchamp (*Ann. Chim. Phys.* 24, 248), Schweigger, Reuss, and Seiler (*Schw.* 39, 386), L. Gmelin (*Pogg.* 7, 451), Kastner (*Kastn. Archiv.* 13, 408; 18, 489), Wanderlich (*Wirtemb. med. Correspond. Blatt.* 1837, 457), Chevalier (*J. Chim. med.* 12, 37).

The cooling of heated bodies in the air and in gases is due, partly to the radiation which takes as it would in vacuo, partly to the immediate transference of heat to the particles of air surrounding the bodies. The latter mode of communication is not affected either by the nature of the surface or by the absolute temperature, provided the difference of temperature between the heated body and the surrounding air remains the same; so long as the elasticity of the air continues unaltered, its density may vary in any way whatever from change of temperature, without producing any alteration in the rate of cooling. On the other hand, the velocity of cooling by contact varies: 1. With the elasticity of the several kinds of gas—inasmuch as the diminution of elasticity consequent on mechanical rarefaction lessens the rate of cooling in a proportion which is different in the different kinds of gas; 2. According to the nature of the surrounding gas—being greatest in hydrogen (whether from the greater mobility of that gas or its greater capacity for heat?) less in olefiant gas, still less in air, still less in carbonic acid, and, according to Davy (*Schw.* 20, 153), slowest of all in chlorine gas. (Similar results are given by Dalton in his *New Syst.* 1, 114.) But even when the actual velocity changes, the law of cooling by contact of gas remains always the same, viz., that when the difference of temperature is doubled, the velocity of cooling increases 2·35 fold. (Petit and Dulong.) *Comp.*, Despretz (*Ann. Chim. Phys.* 6, 184), and Prevost (*Mém. de la Société de Genève*, 4, 265). —Disturbance of the air accelerates the rate of cooling.—The observation of Böckman that metals cool more quickly, and charcoal, earthy substances, and liquids more slowly, when heated in the sun than when heated in the sand-bath, deserves further investigation.

6. Heat which enters into bodies *expands* them. This expansion varies greatly according to the nature of the substance, not only in degree, but also in the law which it follows.

* Thomson, *Nicholson's Phil. Journ.* vol. 4, p. 529 f.
Murray ,, ,, vol. 1, p. 165 and 241.
Dalton, *Memoirs of the Society of Manchester*, vol. 5, part II. p. 373 f.

All *gases* and *vapours*, *e. g.*, common air, oxygen, hydrogen, nitrogen, carbonic acid, hydrochloric acid, and sulphurous acid gas, and ether vapour expand when heated from 0° to 100° C. by 0·375 of their volume, according to Gay-Lussac and Dalton, and from 0·364 to 0·365 according to Rudberg. The latter determination gives an expansion of $\frac{1}{274}$ for each degree centigrade (or $\frac{1}{493}$ for each degree Fah.); that is to say, 274 cubic inches of air at 0° become 275 c. i. at + 1°, 276 c. i. at 2°, and 375 cubic inches at 100°; at 274° their volume is doubled, at 548 it is trebled, and so on. On the contrary, 274 measures of any gas at 0° suffer a contraction of 1 measure for each degree of cooling. 274 measures of gas at 0° contract at − 20° to 254 measures, and expand at + 30° to 304, at + 80° to 354, and at + 100° to 574 measures. Hence the volume of a gas measured at any given temperature may be reduced to the volume which it would have at any other temperature; *e. g.* given 1000 measures at − 14°: required the volume at 0°?—(274 − 14) : 274 = 1000 : x = 1053·8.—Given 1000° measures at + 36° : what is the volume at 0? (274 + 36) : 274 = 1000 : x = 884.—Given 1000 measures at 27° : what will be the volume at 100°? (274 + 27) : (274 + 100) : : 1000 : x = 1242·5.—Even when the heat is increased to 300° C. the expansion of different gases, as of air and hydrogen, is exactly the same. (Petit and Dulong.)—The expansion of atmospheric air when heated from 0° to 100° is constantly the same, whether it be subjected to a pressure of $\frac{1}{14}$, $\frac{1}{6}$, $\frac{1}{3}$, $\frac{1}{2}$, 1, 2, 3, 6, or 15 atmospheres. (Davy, *Phil. Transact.* 1823, 204.)—Common air, heated from 100° to low redness, expands from 1 measure to 2·25, and at a bright red heat to more than 2·50 measures. (Davy.)—According to Muncke, vapours heated to their boiling point expand much more strongly than air.

¶ The more recent experiments of Magnus and Regnault have shown that the coefficient of expansion is not exactly the same for all gases. The differences, however, are not very considerable, as will be seen from the following table, which gives the expansions of the different gases examined by these philosophers, between the temperatures of melting ice and boiling water.

Name.	Expansion.	Obs.	Name.	Expansion.	Obs.
Air	0·36650	Rt.	Carbonic oxide	0·36667	Rt.
,,	0·36651	Mg.	Carbonic acid	0·36896	—
Nitrogen	0·36682	Rt.	,, ,,	0·36909	Mg.
Hydrogen	0·36678	—	Sulphurous acid	0·39028	Rt.
,,	0·36566	Mg.	,, ,,	0·38562	Mg.
Cyanogen	0·36821	Rt.	Hydrochloric acid	0·36812	Rt.

Hence it appears that the expansion of air for each degree centigrade is equal to 0·003665 of the bulk at 0° C.; this gives 0·00204 or $\frac{1}{490}$ for each degree of Fahrenheit's scale.—Regnault also found that for atmospheric air, carbonic acid, and sulphurous acid, the coefficient of expansion increases with the tension of the gas.

The laws commonly admitted,—viz. that *the expansion of any gas between given limits of the temperature is independent of the initial density;* and that *all gases have the same coefficient of expansion*—are regarded by Regnault as true *in the limit only;* that is to say—they accord more and more nearly with the results of observation in proportion as the gases are in a more expanded state. ¶.

Liquids heated from 0° to 100° C. expand as follows.

Water	0·0466	Dalton.	Mercury	0·0200	Dalton
Saturated solution of salt	0·0500			0·01887	Cavendish
Oil of vitriol	0·0600			0·01848	Lavoisier and Laplace
Hydrochloric acid (sp. gr. 1·137)	0·0600				
Nitric acid (sp. gr. 1·40)	0·1100			0·01818	Hallström
Alcohol (sp. gr. 0·817)	0·1100			0·01801	Shuckburgh
Ether	0·0700			0·01800	Petit and Dulong
Oil of turpentine	0·0700			0·01786	Deluc
Fat oil	0·0800			0·01695	Roy.

100 measures of liquid carbonic acid at − 20° expand to 150 measures at + 30. [Such at least is the case according to the assertion of Thilorier (*Ann. Chim. Phys.* 60, 427), that the sp. gr. of this acid is 0·90 at − 20°, 0·83 at 0°, and 0·60 at + 30°; but at the same time he says: 100 measures of the acid at 0° give 145 measures at + 30, which is inconsistent with the above]. It is certain, however, that the expansion of liquid carbonic acid is much greater than that of gases. Likewise, sulphurous acid and cyanogen in the liquid state expand much more strongly than other liquids, but not so much as carbonic acid. (Kemp.)

Water, when gradually heated from its freezing point, contracts at first, and does not expand till its temperature has been raised somewhat higher. If, therefore, it be at the particular temperature at which its density is the greatest, it will expand, whether heat be added to or abstracted from it. This point of maximum density is placed by Dalton at 2·22° C., by Blagden & Gilpin and by Gay-Lussac at 3·89° (39° Fah.), by Hällstrom at 3·9° (*Pogg.* 34, 220), Charles at 3·99°, Despretz at 4°, Hope at 4·35°, Lefevre, Gineau and Rumford at 4·44°, by Crichton at 5·55°, and by Playfair & Joule at 39·101° Fah., or 3·95° C. (*Chem. Mem.* 3, 204.) The apparent maximum density of water enclosed in glass vessels is not attained, according to Dalton, till 5·55°, because the vessel expands when its temperature is raised from 0° to 4°. (For Hällstrom's table of the density of water at different temperatures, vid. *Ann. Chim. Phys.* 28, 56.)

All aqueous solutions of salts and similar substances have likewise, according to Despretz, a maximum of density. This maximum is situated so much the more below 4° as the solution is richer in salt, and generally even below the temperature at which the solution freezes when agitated; whilst the liquid, when at rest, may be cooled below the point of maximum density without assuming the solid form. Solutions of 3·759 parts of the following substances in 100 parts of water have their maxima of density and their freezing points when agitated situated at the following temperatures:

	Max.	Fr. P.		Max.	Fr. P.
Potash	−5·64°	−2·10°	Sulphate of soda	−4·33°	−2·30°
Carb. potash	3·95	3·21	Common salt	4·75	2·77
Sulphate of potash	2·28	2·09	Chloride of calcium	3·92	3·92
Carbonate of soda	7·01	2·85	Dry sulphate of copper	0·62	1·32

¶ The expansion of liquids has lately been further investigated by M. Isidore Pierre: the results of his experiments are contained in a series of memoirs published in the *Annales de Chimie et de Physique*, 3ᵉ *sér.* The following table contains the true and mean coefficients of expansion of

the several liquids examined. The expansions being expressed by formulæ of the form

$$V = 1 + at + bt^2 + ct^3$$

in which t denotes the temperature, and a, b, c are constants to be determined by observation for each particular liquid,—the true coefficients for each temperature are calculated by the formula

$$\frac{dV}{dt} = a + 2bt + 3ct^2$$

and the mean coefficients by the formula

$$\frac{V_t - V_0}{t} = a + bt + ct^2$$

Substances.	Temperatures.	True coefficient.	Mean coefficient.
Wood-spirit	− 35·0	0·001 109 738	0·001 141 901
,,	0·0	0·001 185 570	
,,	63·0	0·001 491 250	0·001 329 747
Fusel-oil	0·0	0·000 890 011	
,,	100·0	0·001 339 328	0·001 068 560
,,	131·8	0·001 606 382	0·001 164 842
Alcohol	− 30·0	0·000 944 782	0·000 997 311
,,	0·0	0·001 048 630	
,,	78·3	0·001 347 576	0·001 195 509
Bromide of ethyl	− 30·0	0·001 290 277	0·001 269 422
,, ,,	0·0	0·001 337 628	
,, ,,	40·7	0·001 540 060	0·001 448 731
Bromide of methyl	0·0	0·001 415 206	
,, ,,	13·0	0·001 559 038	0·001 493 693
Iodide of ethyl	− 30·0	0·001 018 046	0·001 088 924
,, ,,	0·0	0·001 142 251	
,, ,,	70·0	0·001 480 311	0·001 263 687
Iodide of methyl	− 35·0	0·001 085 098	0·001 164 759
,, ,,	0·0	0·001 199 591	
,, ,,	43·8	0·001 446 938	0·001 327 135
Butyric methyl-ether	0·0	0·001 239 896	
,, ,,	102·1	0·001 776 201	0·001 440 012
Butyric ether	0·0	0·001 202 792	
,, ,,	119·0	0·001 534 408	0·001 439 571
Acetic ether	− 40·0	0·001 029 108	0·001 142 608
,, ,,	0·0	0·001 258 496	
,, ,,	74·14	0·001 719 623	0·001 489 001
Acetic methyl-ether	− 30·0	0·001 132 859	0·001 232 491
,, ,,	0·0	0·001 295 954	
,, ,,	59·5	0·001 687 434	0·001 484 159
Terchloride of phosphorus	0·0	0·001 128 619	
,, ,,	78·34	0·001 589 242	0·001 307 358
Terbromide of phosphorus	0·0	0·000 847 205	
,, ,,	100·0	0·001 008 780	0·000 916 249
,, ,,	175·3	0·001 149 896	0·000 986 237
Terchloride of arsenic	− 30·0	0·000 925 854	0·000 951 664
,, ,,	0·0	0·000 979 073	
,, ,,	133·81	0·001 333 299	0·001 140 338
Bichloride of tin	− 25·0	0·001 101 490	0·001 113 945
,, ,,	0·0	0·001 132 801	
,, ,,	115·4	0·001 647 378	0·001 338 953
Bichloride of titanium	− 25·0	0·000 876 944	0·000 909 479
,, ,,	0·0	0·000 942 559	
,, ,,	136·0	0·001 357 899	0·001 142 034
Chloride of silicium	− 40·0	0·001 272 135	0·001 272 094

Substances.	Temperatures.	True coefficient.	Mean coefficient.
Chloride of silicium	0·0	0·001 294 119	
,, ,, ...	59·0	0·001 978 592	0·001 563 537
Bromide of silicium.....	0·0	0·000 952 572	
,, ,, ...	100·0	0·001 112 682	0·001 031 167
,, ,, ...	153·36	0·001 205 180	0·001 053 126
Chloride of acetyl	− 30·0	0·001 084 043	0·001 096 836
,, ,, ...	0·0	0·001 118 932	
,, ,, ...	84·92	0·001 530 055	0·001 282 410
Bromide of acetyl	20·09	0·000 952 696	
,, ,, ...	100·0	0·001 182 181	0·001 064 922
,, ,, ...	132·6	0·001 453 206	0·001 117 913
Bromine	− 7·0	0·001 016 027	0·000 970 284
,, ...	0·0	0·001 038 186	
,, ...	63·0	0·001 318 677	0·001 167 673
Sulphurous acid	− 8·0	0·001 810 947	0·001 737 142
,, ,, ...	− 25·85	0·001 496 377	
Sulphite of oxide of ethyl ..	9·0	0·000 990 479	
,, ,, ,, ..	100·0	0·001 257 739	0·001 157 912
,, ,, ,, ..	160·3	0·001 461 725	0·001 205 933

It will be seen from this table (1) that for all the above liquids, both the mean and true coefficients of expansion increase with the temperature; (2) that for temperatures above 0° the true coefficient is greater than the mean, whereas below 0° it is less; (3) that the true coefficient increases more rapidly than the mean.

In the following table, the volume of the liquids at their boiling point is taken for unity, and the changes of volume are given for all the liquids at equal distances from their boiling points. At the head of each column is given the boiling point of the liquid, together with the barometric pressure at the time of observation.—The results detailed in this table are of especial importance in connection with the equivalent volumes of the several liquids; since, according to Kopp and Schröder, the equivalent volumes of liquids should be compared at temperatures equally distant from their boiling points.

Number of degrees below boiling point.	Wood-spirit *B. P.* 66·3° (*bar.* 759mm).	Alcohol *B. P.* 78·3° (*bar.* 758mm).	Fusel-oil *B. P.* 131·8° (*bar.* 751·26mm)	Acetate of Methyl *B. P.* 59·5° (*bar.* 761·2mm).	Acetic Ether *B. P.* 74·14° (*bar.* 766·5mm).	Butyrate of Methyl *B. P.* 102·1° (*bar.* 743·9mm).
0	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
5	0·9931	0·9938	0·9932	0·9923	0·9922	0·9924
10	0·9863	0·9878	0·9865	0·9848	0·9846	0·9849
15	0·9796	0·9819	0·9800	0·9775	0·9772	0·9777
20	0·9732	0·9761	0·9737	0·9703	0·9700	0·9706
25	0·9669	0·9703	0·9676	0·9633	0·9629	0·9636
30	0·9608	0·9646	0·9617	0·9564	0·9559	0·9569
35	0·9547	0·9590	0·9559	0·9497	0·9491	0·9503
40	0·9488	0·9536	0·9503	0·9431	0·9424	0·9438
45	0·9430	0·9482	0·9448	0·9367	0·9359	0·9375
50	0·9373	0·9429	0·9394	0·9304	0·9295	0·9312
55	0·9316	0·9377	0·9342	0·9243	0·9233	0·9251
60	0·9260	0·9325	0·9292	0·9183	0·9172	0·9192
65	0·9206	0·9275	0·9241	0·9124	0·9112	0·9133
70		0·9225	0·9192	0·9065	0·9053	0·9075

Number of degrees below boiling point.	Alcohol *B. P.* 78·3° (*bar.* 758mm).	Fusel-oil *B. P.* 131·8° (*bar.* 751·26mm)	Acetate of Methyl *B. P.* 59·5° (*bar.* 761·2mm).	Acetic Ether *B. P.* 74·14° (*bar.* 766·5mm).	Butyrate of Methyl *B. P.* 102·1° (*bar.* 743·9mm).
75	0·9176	0·9145	0·9010	0·8996	0·9017
80	0·9128	0·9098	0·8955	0·8940	0·8961
85	0·9081	0·9053	0·8899	0·8886	0·8905
90	0·9034	0·9009	0·8843	0·8833	0·8850
95	0·8989	0·8966	0·8788	0·8781	0·8795
100	0·8945	0·8924		0·8730	0·8741
105	0·8899	0·8882		0·8681	0·8687
110	0·8856	0·8841		0·8633	0·8633
115		0·8801			0·8580
120		0·8761			0·8526
125		0·8722			0·8472
130		0·8683			0·8418
135		0·8644			
140		0·8606			
145		0·8568			

Number of degrees below boiling point.	Butyric Ether *B. P.* 119° (*bar.*747·50mm)	Iodide of Ethyl *B. P.* 70° (*bar.* 751·7mm).	Iodide of Methyl *B. P.* 43·8° (*bar.* 750mm).	Bromide of Methyl *B. P.* 13° (*bar.* 759mm).	Bromide of Ethyl *B. P.* 40·7° (*bar.* 757mm).	Hydrochloric Ether *B. P.* 11° (*bar.* 758mm).
0	1·0000	1·0000	1·0000	1·0000	1·0000	1·000000
5	0·9933	0·9938	0·9934	0·9926	0·9925	0·992370
10	0·9865	0·9875	0·9863	0·9854	0·9853	0·984530
15	0·9795	0·9812	0·9796	0·9784	0·9782	0·977021
20	0·9724	0·9752	0·9733	0·9715	0·9713	0·969827
25	0·9652	0·9691	0·9672	0·9647	0·9643	0·962634
30	0·9583	0·9632	0·9612	0·9579	0·9580	0·955552
35	0·9515	0·9572	0·9552	0·9509	0·9516	0·948538
40	0·9446	0·9514	0·9494	0·9438	0·9452	0·941865
45	0·9378	0·9456	0·9437		0·9389	
50	0·9313	0·9401	0·9381		0·9327	
55	0·9248	0·9346	0·9326		0·9265	
60	0·9185	0·9293	0·9272		0·9204	
65	0·9124	0·9239	0·9218		0·9148	
70	0·9065	0·9187	0·9163		0·9091	
75	0·9007	0·9105	0·9108			
80	0·8950	0·9084				
85	0·8895	0·9034				
90	0·8840	0·8984				
95	0·8787	0·8935				
100	0·8734	0·8887				
105	0·8682					
110	0·8630					
115	0·8579					
120	0·8527					
125	0·8476					
130	0·8424					
135	0·8373					

Number of degrees below boiling point.	Chloride of Acetyl *B. P.* 84·92° (*bar.* 761·88mm).	Bromide of Acetyl *B. P.* 132·6° (*bar.* 756·9mm).	Chloride of Silicium *B. P.* 59° (*bar.* 760·1mm).	Bromide of Silicium *B. P.* 153·36° (*bar.* 760·1mm).	Bichloride of Tin *B. P.* 115·4° (*bar.* 753·1mm).	Bichloride of Titanium *B. P.* 136° (*bar.* 762·3mm).
0	1·000000	1·000000	1·000000	1·000000	1·000000	1·000000
5	0·993229	0·994056	0·991277	0·995575	0·992952	0·994194
10	0·986610	0·988308	0·982831	0·990872	0·986047	0·988397
15	0·980059	0·982702	0·974791	0·986197	0·979286	0·982706
20	0·973833	0·977212	0·967158	0·981671	0·972663	0·977081
25	0·967653	0·971801	0·959631	0·976969	0·966173	0·971532
30	0·961604	0·966456	0·952517	0·972374	0·959732	0·966053
35	0·955680	0·961279	0·945665	0·967671	0·953566	0·960645
40	0·949854	0·956151	0·939049	0·962739	0·947453	0·955306
45	0·944157	0·951030	0·932638	0·957789	0·941455	0·950037
50	0·938579	0·945978	0·926407	0·952951	0·935553	0·944836
55	0·933080	0·940980	0·920327	0·948163	0·929760	0·939635
60	0·927671	0·936063	0·914366	0·943402	0·924067	0·934713
65	0·922344	0·931211	0·908502	0·938680	0·918466	0·929664
70	0·917091	0·926421	0·902744	0·933992	0·912956	0·924710
75	0·911907	0·921710	0·896944	0·929340	0·907530	0·919844
80	0·906784	0·917055	0·891194	0·924723	0·902182	0·915044
85	0·901715	0·912454	0·885427	0·920142	0·896918	0·910309
90	0·896691	0·907917	0·879613	0·915596	0·891691	0·905638
95	0·891710	0·903446	0·873726	0·911085	0·886566	0·901032
100	0·886760	0·899036		0·906608	0·881488	0·896485
105	0·881838	0·894686		0·902165	0·876464	0·892002
110	0·876935	0·890396		0·897756	0·871488	0·887582
115		0·886135		0·893386	0·866550	0·883222
120				0·889048	0·861669	0·878923
125				0·884742	0·856813	0·874684
130				0·880470	0·851988	0·870505
135				0·876222	0·847188	0·866383
140				0·872027	0·842424	0·862323
145				0·867856	0·837643	0·858319
150				0·863717		
155						

Number of degrees below boiling point.	Terbromide of Phosphorus *B. P.* 175·3° (*bar.* 760·2mm).	Terchloride of Phosphorus *B. P.* 78·34° (*bar.* 751·5mm).	Terchloride of Arsenic *B. P.* 133·81° (*bar.* 756·1mm).	Bromine *B. P.* 63° (*bar.* 760·02mm)	Sulphurous acid *B. P.* 8° (*bar.* 759·18mm)	Sulphite of oxide of Ethyl *B. P.* 160·3° (*bar.* 763·76mm)
0	1·000000	1·000000	1·000000	1·000000	1·000000	1·000000
5	0·995103	0·992876	0·994252	0·993936	0·996457	0·994299
10	0·990266	0·985971	0·988576	0·987981	0·987128	0·987627
15	0·985467	0·979272	0·982970	0·982146	0·979060	0·981906
20	0·980705	0·972567	0·977434	0·976128	0·971174	0·976297
25	0·975982	0·966444	0·971967	0·970822	0·969925	0·970600
30	0·971221	0·960290	0·966566	0·965287	0·964270	0·964811
35	0·966654	0·954294	0·961232	0·959875		0·959199
40	0·962050	0·948443	0·955961	0·954676		0·953586
45	0·957496	0·942725	0·950751	0·949538		0·948076

Number of degrees below boiling point.	Terbromide of Phosphorus *B. P.* 175·8° (*bar.* 760·2mm).	Terchloride of Phosphorus *B. P.* 78·34° (*bar.* 751·5mm).	Terchloride of Arsenic *B. P.* 133·81° (*bar.* 756·1mm).	Bromine *B. P.* 63° (*bar.* 760·02mm)	Sulphite of oxide of Ethyl *B. P.* 160·3° (*bar.* 763·76mm)	
50	0·952975	0·937128	0·945611	0·944399	0·942637	
55	0·948494	0·931640	0·940528	0·9393.4	0·937264	
60	0·944052	0·926248	0·935504	0·934406	0·931959	
65	0·939650	0·920941	0·930543	0·929562	0·926717	
70	0·935288	0·915707	0·925638	0·924652	0·921537	
75	0·930965	0·910531	0·920789		0·916427	
80	0·926672	0·905403	0·915996		0·911375	
85	0·922437	0·900311	0·911257		0·906383	
90	0·918249	0·895243	0·906571		0·901454	
95	0·914107	0·890185	0·901938		0·896583	
100	0·910011	0·885129	0·897351		0·891779	
105	0·905956	0·880063	0·892809		0·887045	
110	0·901944	0·874958	0·888338		0·882318	
115	0·897969	0·869803	0·883902		0·877671	
120					0·873075	
125					0·868546	
130					0·864063	
135					0·859638	
140					0·855252	
145					0·850920	
150					0·846638	
155					0·842403	
160					0·838214	

It will be seen from these tables: I. That a nearly equal contraction from the boiling point downwards is exhibited by: (1). Fusel-oil, wood-spirit and alcohol; (2). Bromide of ethyl and bromide of methyl; (3). Iodide of methyl and iodide of ethyl; (4). Acetic ether and acetic methyl-ether; (5). Butyric ether and butyric methyl-ether.

II. That this equal contraction from the boiling point downwards does not extend to all groups of liquids containing a common element united with different isomorphous elements (*e. g.* chloride of phosphorus and chloride of arsenic), but appears to be confined to the ethyl and methyl series.

III. That in each group of liquids the difference of contraction increases constantly in the same direction, in proportion as the temperature falls below the boiling point.

IV. This difference of contraction attains in some cases a very considerable magnitude; *e. g.* in the group consisting of the bromide and chloride of silicium it amounts to half the total expansion of one of these liquids.

V. In each group, the liquid which has the lowest boiling point expands and contracts the most. This observation must not however be extended to liquids belonging to different groups.

Kopp has also published an elaborate series of researches on the expansion of liquids. (*Pogg.* 72, 1 and 223; abstr. *Ann. Chem. Pharm.* 64, 212.)—The following are the results obtained with regard to the expansion of water, the volume at 0° being taken for unity.

Temp.	Volume.	Temp.	Volume.	Temp.	Volume.
0°	1·000000	14°	1·000556	40°	1·007531
1	0·999947	15	1·000695	45	1·009541
2	0·999908	16	1·000846	50	1·011766
3	0·999885	17	1·001010	55	1·014100
4	0·999877	18	1·001184	60	1·016590
5	0·999883	19	1·001370	65	1·019302
6	0·999903	20	1·001567	70	1·022246
7	0·999938	21	1·001776	75	1·025440
8	0·999986	22	1·001995	80	1·028581
9	1·000048	23	1·002225	85	1·031894
10	1·000124	24	1·002465	90	1·035397
11	1·000213	25	1·002715	95	1·039094
12	1·000314	30	1·004064	100	1·042986
13	1·000429	35	1·005697		

The expansions of the other liquids examined by Kopp are given in the following table, the volume of each liquid at 0° C. being taken as unity. The densities ($= d$) reduced to 0°, and the boiling points under a pressure corresponding to 760^{mm} or 29·92 inches of the barometer are also given at the heads of the respective columns. ¶.

Temp.	Wood-spirit $d = 0{\cdot}8180$ B.P. $= 65{\cdot}5°$	Alcohol $d = 0{\cdot}8095$ B.P. $= 78{\cdot}4°$	Fusel-oil $d = 0{\cdot}8253$ B.P. $= 131{\cdot}1°$	Ether $d = 0{\cdot}7366$ B.P. $= 34{\cdot}9°$	Aldehyd $d = 0{\cdot}8009$ B.P. $= 20{\cdot}8°$	Acetone $d = 0{\cdot}8144$ B.P. $= 56{\cdot}3°$	Benzol $d = 0{\cdot}8991$ B.P. $= 80{\cdot}4°$	Formic acid $d = 1{\cdot}2227$ B.P. $= 105{\cdot}3°$	Acetic acid $d = 1{\cdot}0805$ B.P. $= 117{\cdot}3°$
0	1·00000	1·00000	1·00000	1·00000	1·00000	1·00000	1·00000	1·00000	1·00000
5	1·00576	1·00523	1·00454	1·00750	1·00790	1·00680	1·00529	1·00497	1·00529
10	1·01154	1·01052	1·00911	1·01518	1·01616	1·01387	1·01190	1·01000	1·01060
15	1·01734	1·01585	1·01373	1·02308	1·02476	1·02085	1·01796	1·01505	1·01588
20	1·02319	1·02128	1·01840	1·03122	1·03372	1·02810	1·02410	1·02016	1·01129
25	1·02912	1·02680	1·02311	1·03962		1·03551	1·03033	1·02530	1·02669
30	1·03513	1·03242	1·02790	1·04829		1·04310	1·03665	1·03050	1·03213
35	1·04124	1·03817	1·03278	1·05726		1·05087	1·04308	1·00577	1·03764
40	1·04751	1·04404	1·03773			1·05884	1·04961	1·04109	1·04319
45	1·05391	1·05006	1·04280			1·06700	1·05625	1·04648	1·04881
50	1·06049	1·05623	1·04797			1·07538	1·06302	1·05194	1·05451
55	1·06726	1·06257	1·05327			1·08396	1·06900	1·05748	1·06030
60	1·07425	1·06910	1·05869			1·09278	1·07692	1·06310	1·06617
65	1·08147	1·07584	1·06425				1·08407	1·06880	1·07213
70		1·08278	1·06998				1·09136	1·07460	1·07820
75		1·08994	1·07586				1·09880	1·08048	1·08438
80		1·09735	1·08192				1·10641	1·08647	1·09067
85			1·08815				1·11412	1·09255	1·09709
90			1·09458					1·09875	1·10364
95			1·10122					1·10507	1·11033
100			1·10808					1·11148	1·11717
105			1·11515					1·11803	1·12417
110			1·12245						1·13133
115			1·13001						1·13865
120			1·13783						1·14614
125			1·14589						
130			1·15426						
135			1·16290						

Temp.	Butyric acid $d = 0{\cdot}9886$ B.P. $= 157{\cdot}0°$	Formiate of methyl $d = 0{\cdot}9884$ B.P. $= 33{\cdot}4°$	Formic ether $d = 0{\cdot}9447$ B.P. $= 54{\cdot}9°$	Acetate of methyl $d = 0{\cdot}9562$ B.P. $= 56{\cdot}3°$	Acetic ether $d = 0{\cdot}9105$ B.P. $= 74{\cdot}3°$	Butyrate of methyl $d = 0{\cdot}9210$ B.P. $= 95{\cdot}9°$	Butyric ether $d = 0{\cdot}9041$ B.P. $= 114{\cdot}8°$	Valerianate of methyl B.P. $= 116{\cdot}2°$
0	1·00000	1·00000	1·00000	1·00000	1·00000	1·00000	1·00000	1·00000
5	1·00525	1·00707	1·00683	1·00649	1·00642	1·00603	1·00592	1·00565
10	1·01052	1·01428	1·01369	1·01317	1·01297	1·01216	1·01193	1·01108
15	1·01583	1·02162	1·02062	1·02004	1·01964	1·01837	1·01800	1·01721
20	1·02117	1·02916	1·02766	1·02710	1·02644	1·02471	1·02417	1·02315
25	1·02659	1·03692	1·03481	1·03435	1·03340	1·03113	1·03042	1·02919
30	1·03203	1·04495	1·04211	1·04179	1·04050	1·03776	1·03678	1·03532
35	1·03754	1·05326	1·04960	1·04940	1·04778	1·04449	1·04325	1·04158
40	1·04309		1·05730	1·05719	1·05521	1·05135	1·04983	1·04794
45	1·04871		1·06525	1·06517	1·06283	1·05836	1·05654	1·05444
50	1·05439		1·07347	1·07331	1·07064	1·06554	1·06338	1·06105
55	1·06013		1·08199	1·08161	1·07865	1·07287	1·07035	1·06779
60	1·06596				1·08686	1·08037	1·07747	1·07467
65	1·07187				1·09529	1·08806	1·08474	1·08168
70	1·07785				1·10395	1·09594	1·09216	1·08884
75	1·08391				1·11284	1·10400	1·09975	1·09615
80	1·09007					1·11226	1·10753	1·10360
85	1·09631					1·12074	1·11548	1·11122
90	1·10266					1·12944	1·12361	1·11898
95	1·10910					1·13835	1·13193	1·12691
100	1·11565					1·14750	1·14407	1·13503
105	1·12231						1·14921	1·14330
110	1·12909						1·15816	1·15175
115	1·13598						1·16914	1·16038
120	1·14299							1·16920
125	1·15013							
130	1·15741							
135	1·16481							
140	1·17235							
145	1·18003							
150	1·18786							
155	1·19584							
160	1·20399							

Linear expansion of *Solid bodies* when heated from 0° to 100° C.*

Black marble (Lucullite)	0·00035300	= $\frac{1}{2833}$	Dunn & Sang
Carrara marble	0·00083700	= $\frac{1}{1193}$	,, ,,
White glass in tubes	0·00089694	= $\frac{1}{1115}$	Lavoisier & Laplace
Flint-glass	0·00081166	= $\frac{1}{1148}$	,, ,,
Earthenware	0·00083000	= $\frac{1}{1200}$	Dalton
Brown Fayence	0·00040000	= $\frac{1}{2500}$	,,
Antimony	0·00108333	= $\frac{1}{923}$	Smeaton
Bismuth	0·00139167	= $\frac{1}{719}$	,,
Zinc (cast)	0·00294167	= $\frac{1}{340}$	,,
—— (hammered)	0·00310833	= $\frac{1}{322}$	,,
Malacca tin	0·00193765	= $\frac{1}{516}$	Lavoisier & Laplace

* The linear expansion of a solid multiplied by 3 gives the expansion in volume, very nearly.

Lead	0·00284836	= $\frac{1}{351}$	Lavoisier & Laplace
Iron wire	0·00123504	= $\frac{1}{809}$	,, ,,
Copper	0·00171733	= $\frac{1}{582}$	,, ,,
Brass wire	0·00193337	= $\frac{1}{517}$	Smeaton
Silver	0·00190868	= $\frac{1}{524}$	Lavoisier & Laplace
Gold	0·00155155	= $\frac{1}{644}$	,, ,,
Platinum	0·0009918	= $\frac{1}{1008}$	Troughton
Palladium	0·0010000	= $\frac{1}{1000}$	Wollaston

Crystals not belonging to the regular system exhibit when heated an unequal expansion in the direction of their axes, in consequence of which the magnitude of their angles becomes altered (Mitscherlich, *Pogg.* 1, 125; 10, 137). In crystals belonging to the right prismatic system the expansion is different in the direction of all three axes; in arragonite, on raising the temperature from 0 to 100°, the inclination of the lateral faces increases by 2′ 46″, and that of the terminal faces diminishes by 5′ 29″; gypsum is, according to Fresnel (*Bull. des Sc. Mathem.* 1824, 100; also *Pogg.* 2, 109), more expanded by heat in the direction of the principal axes than in that of the lateral axes.—In crystals belonging to the rhombohedral system the expansion is the same in the directions of the three secondary axes; but different from that according to the principal axis. The obtuse angles of the primitive rhombohedron of calcspar diminish by 8½′ when the crystal is heated 100°, and the acute angles increase by the same quantity. Hence it may be calculated that the relative expansion of the principal axis (compared with the secondary axes) amounts to 0·00342; moreover since, according to Mitscherlich and Dulong, the cubical expansion of calcspar between 0° and 100° is only 0·001961, it may likewise be determined that calcspar, when thus heated, does not expand in the direction of the secondary axes, but *contracts* by 0·00056, and that the absolute expansion of the principal axis may be estimated at 0·00286.—In bitter-spar, the obtuse angle of the primitive rhombohedron diminishes when the temperature is raised from 0° to 100° by 4′ 6″; in ferruginous bitter-spar, by 3′ 29″; in iron spar, containing a considerable quantity of manganese, by 3′ 31″; and in pure iron spar, by 2′ 22″. Since now, among all these minerals, calcspar forms the least, and ferruginous bitter-spar the most obtuse rhombohedron, it follows that the expansion in the direction of the principal axis does not increase in the same proportion as the relative length of the axis itself diminishes. (Mitscherlich.)

The alloy of 2 parts bismuth, 1 part tin, and 1 part lead, expands when heated from 0° to 44° C.; when still further heated it contracts, so that at 56° its density is the same as it was at 0°, and at 69° still greater; beyond this temperature, expansion again takes place; at 87·5° the alloy has once more the same density as at 0°; and at 94°, at which it fuses, the same as at 44°. (Erman, *Pogg.* 9, 557.)

For an account of H. Schröder's attempt to discover a relation between the equivalent volume and the expansion of bodies, see *Pogg.* 52, 282.

¶ Messrs. Playfair & Joule have lately made some experiments on the expansion of salts and other solid bodies. (*Qu. J. of Chem. Soc.* I. 121.) The results are as follows:

Name.	Formula.	Expansion for 180° Fah.
Copper (*reduced by hydrogen*)	Cu	0·0055
,, ,, ...	,,	0·00767
Red oxide of mercury	Hg O	0·005802
Protoxide of lead	Pb O	0·00795
Red oxide of manganese	$Mn^3 O^4$	0·00522
Peroxide of tin	$Sn O^2$	0·00172
Sulphuret of lead	Pb S	0·01045
Chloride of potassium	K Cl	0·010944
Chloride of barium	Ba Cl + 2H O	0·009873
Chloride of ammonium	$N H^4$ Cl	0·0191
Nitrate of soda	Na O, $N O^5$	0·0128
Nitrate of potash	K O, $N O^5$	0·01967
Ditto (*in large crystals*)	,,	0·017237
Ditto (*finely powdered*)	,,	0·019487
Nitrate of lead	Pb O, $N O^5$	0·00839
Nitrate of baryta	Ba O, $N O^5$	0·004523
Chlorate of potash	K O, $Cl O^5$	0·017112
Chromate of potash	K O, $Cr O^3$	0·01134
Ditto (*in fine small crystals*)	,,	0·011005
Bichromate of potash	K O, $2Cr O^3$	0·0122
Bichromate of chloride of potassium	K Cl, $2Cr O^3$	0·015902
Oxalic acid	H O, $C^2 O^3$ + 2H O	0·027476
Oxalate of potash	K O, $C^2 O^3$ + H O	0·01162
Binoxalate of potash	K O, $2C^2 O^3$ + 3H O	0·011338
Quadroxalate of potash	K O, $4C^2 O^3$ + 7H O	0·015916
Oxalate of ammonia	$N H^4$ O, $C^2 O^3$ + H O	0·00876
Binoxalate of ammonia	$N H^4$ O, $2C^2 O^3$ + 3H O	0·013718
Quadroxalate of ammonia	$N H^4$ O, $4C^2 O^3$ + 7H O	0·014347
Sulphate of potash	K O, $S O^3$	0·010697
Bisulphate of potash	K O, $S O^3$ + H O, $S O^3$	0·012287
Sulphate of ammonia	$N H^4$ O, $S O^3$ + H O	0·010934
Sulphate of copper	Cu O, $S O^3$ + 5H O	0·009525
,, ,, ...	,,	0·005315
,, ,, ...	,,	0·00812
Sulphate of iron	Fe O, $S O^3$ + 7H O	0·01153
Sulphate of magnesia	Mg O, $S O^3$ + 7H O	0·01019
Sulphate of copper and ammonia ..	Cu O, $S O^3$ + $N H^4$ O, $S O^3$ + 6H O	0·0066113
Sulphate of copper and potash	Cu O, $S O^3$ + K O, $S O^3$ + 6H O	0·009043
Sulphate of magnesia and potash ..	Mg O, $S O^3$ + K O, $S O^3$ + 6H O	0·009372
Chrome alum	$Cr^2 O^3$, $3S O^3$ + K O, SO^3 + 24H O	0·005242
Potash alum	$Al^2 O^3$, $3S O^3$ + K O, SO^3 24H O	0·003682
Sulphate of zinc and potash	Zn O, $S O^3$ + K O, $S O^3$ + 6H O	0·008235
Sulphate of magnesia and ammonia	Mg O, $S O^3$ + $N H^4$ O, $S O^3$ + 6H O	0·007161
Cane sugar	$C^{12} H^{11} O^{11}$	0·011160
Sugar of milk	$C^{12} H^{12} O^{12}$	0·009111

Of the three specimens of sulphate of copper mentioned in the preceding table, the first and third were prepared for experiment by pounding the salt finely and pressing it between folds of bibulous paper. The second was in small crystals, obtained by stirring the cupreous solution while cooling: it contained rather more than 5 equivalents of water.

The expansion of oxalic acid appears to be greater and that of peroxide of tin less than that of any other solid yet examined. ¶.

Since elastic fluids are in so many respects—particularly with regard to their combination in equal proportions by volume—the most normal substances in existence; since they appear to possess no cohesion, which

force probably exerts a disturbing action on the expansion by heat of liquids and solids; since again they all expand in the same ratio between the same limits of temperature, it may in all probability be supposed that their expansion is likewise *uniform;* that is to say, if the addition of any given quantity of heat has produced an expansion of 0·001 for example, the addition of a second equal quantity will produce an increase of exactly 0·001 of the first volume. This being admitted, it is found that all other bodies, when their expansion is compared with that of air, exhibit a *variable expansion*, inasmuch as the expansion produced in them by equal increments of heat is greater at higher than at lower temperatures. If the increase in volume which different bodies undergo between the temperatures of freezing and boiling water be divided into 100 equal parts or degrees, it will be found that when these several bodies are further heated, their expansions will be expressed by different numbers of such parts, and in the following proportion:

	According to Dulong and Petit.					According to Rudberg.	
Air.	Mercury.	Platinum.	Copper.	Iron.	Glass.	Air.	Mercury.
						− 35·96	− 36
0	0	0	0	0	0	0	0
						+ 50·04	+ 50
100	100	100	100	100	100	100	100
150	151·3						
200	204·6					198·81	200
250	255·1						
300	314·15	311·6	328·8	372·6	352·9	294·73	300
350	360						

Dulong and Petit estimated the expansion of air at 0·375 (page 224); Rudberg (*Jahresber.* 19, 44), from his own experiments, determined it to be 0·364; this however will not explain all the deviations. (*Comp.* Pambour, *Compt. rend.* 12, 655; also *Pogg.* 53, 234.)

Expansion by heat serves as the basis of most *Thermometers* which are used to measure the lower degrees of temperature, and of *Pyrometers* by which higher temperatures are indicated. Since gases and vapours are the only bodies whose expansion is uniform, the ordinary thermometers, which are filled with mercury or spirit, cannot give the true temperature exactly, but, on the contrary, always make the higher temperatures too great; moreover, they do not agree among themselves. (The reduction of the degrees of a mercury, platinum, copper, or iron thermometer is, to a certain extent, given in the preceding table.) Again, in using fluids, the expansion of the glass in which they are contained must be taken into consideration, since it makes their apparent less than their real expansion; and since, according to the above table, the expansion of glass at high temperatures increases much more rapidly than that of gases, the error of the mercurial thermometer is to a certain extent corrected by this circumstance. Bellani (*Brugn. Giorn.* 15, 268; 16, 217 and 294) has likewise shown that the bulbs of mercurial thermometers generally contract in the course of time, so that when they are immersed in melting ice, the mercury stands from $\frac{1}{2}$° to 1° R. above the freezing point previously marked; an effect which—as observed by Flaugergues (*Ann. Chim. Phys.* 21, 333) and by Aug. de la Rive & F. Marcet (*Bibl. univ.* 22, 265)—may be attributed to the pressure of the external air on the bulb of the thermometer, inasmuch as there is a

vacuum in the instrument above the mercury. *Vid.* also Von Yelin (*Kastn. Archiv.* 3, 109), Kämtz (*Schw.* 40, 200), Egen (*Pogg.* 11, 276, 335 and 517; 13, 33), Legrand (*Ann. Chim. Phys.* 63, 368), Despretz (*Ann. Chim. Phys.* 64, 312; also *Pogg.* 41, 58), Rudberg (*Pogg.* 40, 39, and 162), and Henrici. (*Pogg.* 50, 251).

¶ Person has found that when thermometers are exposed to temperatures above 300° or thereabout, the shifting of the zero point is much greater than has been hitherto supposed. Despretz had found it to amount to half a degree in 4 or 5 years under ordinary circumstances. Person finds that at the temperatures just mentioned it sometimes reaches from 12° to 17° in a few hours. (*Pogg.* 65, 370.) ¶.

In the common *Air-thermometer*, the air is enclosed in a glass bulb having a tube attached to it, and the tube is closed with a drop of some liquid not easily volatile, such as oil of vitriol. (Gay-Lussac, *Pogg.* 27, 435; Pouillet, *Pogg.* 41, 144.)—In the *Differential Thermometer* or *Photometer* the air is contained in two glass bulbs, connected by a tube bent like a U; a small quantity of liquid contained in the tube is driven backwards and forwards accordingly as one or the other of the bulbs is more strongly heated, and thus shows differences of temperature, but no exact degrees. If one bulb is covered with lamp-black, and the other with gold leaf, the former becomes more strongly heated by exposure to light than the latter, and thus the instrument serves to measure the intensity of light. (Leslie.) The differential thermometer possesses still greater delicacy when filled with vapour of alcohol in contact with excess of alcohol instead of air. (Howard.)—The *Air-pyrometer* is a hollow sphere of platinum fitted with an escape-tube. The hotter the fire to which the platinum vessel is exposed, the greater is the quantity of air driven out of it, and this is received over water and measured. (Pouillet, *Pogg.* 39, 367; also *Elémens de Physique et de Météorologie*, 3^{me} Ed. tom I. p. 351.) —The mercurial thermometer serves for temperatures between + 350° and — 38°; the spirit-thermometer from + 70° to the greatest known degree of cold: for alcohol has never yet been frozen.—In Breguet's *Metallic Thermometer*, three very fine strips of platinum, gold, and silver are laid on one another, and wound into a spiral, which becomes twisted by the unequal expansion and contraction of these metals arising from changes of temperature, and gives motion to an index: this instrument serves not so much for exact measurement of temperatures as, on account of its thinness, for the detection of very transient changes of temperature (*Ann. Chim. Phys.* 5, 312; more shortly in *Schw.* 20, 465.)—The *Metal Pyrometer* consists of a bar of silver, or for higher temperature of platinum, contained in a tube of porcelain, or of clay mixed with black lead. The metallic bar expands more strongly when heated than the clay, and gives motion to an index traversing a graduated arc. (*Vid.* Daniell, *Qu. J. of Sc.* 12, 309; abstr. *Schw.* 32, 497.)

Reaumur divides the interval between the temperatures of melting ice and boiling water into 80, Celsius into 100*, Delisle into 150, and Fahrenheit into 180 equal parts. The first two place the zero at the temperature of melting ice, Delisle at the boiling point of water, Fahrenheit 32° below the melting point of ice: 9° F. = 7·5° D. = 5° C. = 4° R. A correction must be made for the different positions of the zero.

* The temperatures given in this work (except when otherwise specially mentioned) refer to the Centigrade scale.

R +	C +	F +	R +	C +	F +	R +	C +	F +	R +	C +	F +	R −	C −	F +
320	400	752	240	300	572	160	200	392	80	100	212	4	5	23
316	395	743	236	295	563	156	195	383	76	95	203	8	10	14
312	390	734	232	290	554	152	190	374	72	90	194	12	15	5
308	385	725	228	285	545	148	185	365	68	85	185	14·32	17·78	0
304	380	716	224	280	536	144	180	356	64	80	176	16	20	− 4
300	375	707	220	275	527	140	175	347	60	75	167	20	25	13
296	370	698	216	270	518	136	170	338	56	70	158	24	30	22
292	365	689	212	265	509	132	165	329	52	65	149	28	35	31
288	360	680	208	260	500	128	160	320	48	60	140	32	40	40
284	355	671	204	255	491	124	155	311	44	55	131	36	45	49
280	350	662	200	250	482	120	150	302	40	50	122	40	50	58
276	345	653	196	245	473	116	145	293	36	45	113	44	55	67
272	340	644	192	240	464	112	140	284	32	40	104	48	60	76
268	335	635	188	235	455	108	135	275	28	35	95	52	65	85
264	330	626	184	230	446	104	130	266	24	30	86	56	70	94
260	325	617	180	225	437	100	125	257	20	25	77	60	75	103
256	320	608	176	220	428	96	120	248	16	20	68	64	80	112
252	315	599	172	215	419	92	115	239	12	15	59	68	85	121
248	310	590	168	210	410	88	110	230	8	10	50	72	90	130
244	305	581	164	205	401	84	105	221	4	5	41	76	95	139
									0	0	32	80	100	148

a.	*b.*	*c.*	*d.*	*e.*	*f.*
1° R. = 1·25° C.	= 2·25° F.	1° C. = 0·8° R.	= 1·8° F.	1° F. = 0·55° C.	= 0·44° R.
2 = 2·5	= 4·5	2 = 1·6	= 3·6	2 = 1·11	= 0·88
3 = 3·75	= 6·75	3 = 2·4	= 5·4	3 = 1·67	= 1·33
		4 = 3·2	= 7·2	4 = 2·22	= 1·77
				5 = 2·78	= 2·22
				6 = 3·33	= 2·66
				7 = 3·89	= 3·11
				8 = 4·44	= 3·55

How many degrees Fah. = 273° Cels.? According to the table, 270° C. = 518° F.; the 3° C. over are equal by *d.* to 5·4° Fah.; and these added give 518° + 5·4° = 523·4 Fah.—How many degrees of Cels. = 676° Fah.? By the table, 671° F. = 355° C.; and by *d.* 5° F. = 2·78° C., therefore together 671° F. = 355° + 2·78° = 357·78° C.

Wedgewood's Pyrometer depends upon the contraction of cylinders of clay at high temperatures. The first degree W. corresponds, according to Wedgewood, to 598° C., and each degree W. is equal, according to the same authority, to 72° C. According to Guyton-Morveau, on the other hand, the first degree W. corresponds to 270° C., and each degree W. is equal to only 34° C. This pyrometer appears to give but very uncertain indications, the inaccuracy arising chiefly from this circumstance—that the clay cylinders contract as much at a low red heat continued for some time as at a more powerful heat sustained but for a short time.

Prinsep (*Ann. Chim. Phys.* 41, 247) makes alloys of silver and gold, ten parts of which contain 1, 2, 3, 4, 5, 6, 7, 8, or 9 parts of gold;—and for very high temperatures, alloys of gold and platinum containing 99, 98, 97, &c. per cent. of gold; they are made into flattened buttons. These alloys he places in separate cupels in the fire whose strength is to be determined, and ascertains which of them are fused. From a compa-

rative estimation with an air-pyrometer made of gold, it appears that silver melts at 999° C.; 9 parts of silver and 1 of gold at 1049°; 8 silver and 2 gold at 1070°; 6 silver with 4 gold at 1099°; and 3 silver with 7 gold at 1379°. An alloy containing 30 parts gold and 70 platinum is infusible even in the strongest blast furnace.

7. Heat imparts to many ponderable bodies particular colours which vary according to the quantity of heat contained in the bodies. Whenever such bodies are heated, they assume a colour different from that which distinguishes them in the cold; but on cooling again, the original colour reappears. This change of colour is not accompanied by any chemical change.

This appearance is presented by the following liquids, and by the under-mentioned solids in the state of powder.

Sulphur, which at ordinary temperatures is pale pellow, acquires a brownish yellow colour when heated just below its melting point.—Hyponitric acid is colourless at − 20°, pale yellow at 0°, orange yellow at + 20°, and its vapour becomes darker the hotter it is.—Titanic, tantalic and molybdic acids, which are white at common temperatures, become of a lemon-yellow colour when they are heated; lemon-yellow tungstic acid becomes orange-yellow when heated,—green oxide of chromium becomes brown,—orange-coloured chromic acid, red,—pale grey anhydrous tersulphate of chromium, peach-blossom colour,—lemon-yellow neutral chromate of potash or soda, aurora-coloured,—orange-coloured bisulphuret of arsenic, red brown,—lemon-yellow tersulphuret of arsenic, of a colour varying from orange to red brown,—white oxide of antimony and white antimonious acid, lemon-yellow,—pale yellow antimonic acid, brownish yellow,—lemon-yellow oxide of bismuth, of a colour varying from orange to red brown,—very pale yellow oxide of zinc, lemon-yellow,—orange yellow sulphuret of cadmium, first brownish, then crimson red,—yellowish white peroxide of tin, orange-yellow,—yellow oxide of lead, brown-red,—scarlet-red minium, violet-coloured,—yellow chromate of lead, brownish,—brown-red peroxide of iron, dark brown,—colourless aqueous solution of acid pernitrate of iron, reddish yellow,—red sub-oxide of copper, brownish grey,—brownish black protoxide of copper, deep black,—tile-red oxide of mercury, brownish black,—scarlet cinnabar, carmine-red,—white protosulphate of mercury, first yellow, then red,—yellow basic protonitrate of mercury, red,—and yellow di-iodide of mercury, red.

Elevation of temperature then always imparts a darker colour, and generally yellow or brown. Schönbein (*Pogg.* 45, 263) suggests that heat may produce an incipient decomposition, which however does not go so far as the separation of any of the elements; thus red oxide of mercury may when heated assume the brown-black colour of the suboxide from losing a part of its oxygen, which however is retained in a peculiar manner in the mass,—and so forth. It is not however every change of colour that will accord with this hypothesis.

8. The heat which diffuses itself through ponderable bodies accumulates in them in quantities which differ according to their peculiar nature, whether we compare them with regard to weight or volume. Different bodies require different quantities of heat to raise their temperature equally, and disengage unequal quantities of heat in cooling through the same number of degrees of temperature. This different *Capacity* of bodies for heat is called *Specific Heat* when the bodies are compared with regard to their weight, and *Relative Heat* when they are compared with regard

to volume. The specific heat multiplied into the specific gravity gives the relative heat.

When bodies of different temperatures and different capacities for heat are mixed together, the temperature of the mixture is not the mean between the temperatures of the individual substances. Equal weights of bodies equally heated or equally cooled, but of different capacities for heat, raise or lower the temperature of a given quantity of water through different numbers of degrees. Or they melt unequal quantities of ice at 0°. Spheres of equal size and equally heated, but of substances having different capacities for heat, require different times to cool to the same point in the same medium—the radiating power of the surfaces being either accounted for or made the same in all. Gases enclosed in a manometer placed in a warmer medium require different times to produce in them the same amount of expansion by heat. The first of these methods was adopted by Wilke, Crawford, Kirwan, Dalton and Potter; the second by Delaroche & Bérard, Avogadro, Neumann, Regnault; the third particularly by Lavoisier & Laplace with their *calorimeter;* the fourth by Mayer, Böckmann, Petit & Dulong, Hermann, De la Rive & Marcet; the fifth by De la Rive & Marcet,—for the determination of the specific heats of bodies.—Moreover, with regard to the specific heats of gases, Dulong availed himself of the velocity of sound, by causing the gases to blow into a flute and determining the pitch of the sound,—and Suermann, of the cooling produced by the evaporation of water in a stream of the gas.

Specific Heat of Elastic Fluids at the ordinary Pressure of the Atmosphere.

	Specific Heat.		Relative Heat.	
	that of water = 1	that of air = 1	that of air = 1	
Air	0·2500	1·0000	1·0000	Clement & Desormes.
	0·2669			De la Roche & Bérard.
	0·3046			Suermann.
Oxygen gas	0·1956	0·7328	0·8080	Apjohn.
	0·2361	0·8848	0·9765	De la Roche & Bérard.
	0·2750	0·9028	0·9954	Suermann.
		0·9069	1·0000	Clem. & Des., De la Rive & Marcet, Haykraft, Dulong.
Hydrogen gas		9·5774	0·6640	Clement & Desormes.
	3·2936	12·3401	0·9033	De la Roche & Bérard.
		14·423	1·0000	De la Rive & Marcet, Haykraft, Dulong.
	6·1892	20·3191	1·3979	Suermann.
		21·2064	1·4590	Apjohn.
Chlorine gas		0·4074	1·0000	De la Rive & Marcet.
Nitrogen gas	0·2754	1·0318	1·0000	De la Roche & Berard.
	0·3138	1·0293	1·0005*	Suermann.
		1·0741	1·0480	Apjohn.
Vapour of water	0·8470	3·1360	1·9600	De la Roche & Bérard.
Carbonic oxide gas	0·3123	1·0253	0·9925	Suermann.
		1·0239	0·9960	Apjohn.
		1·0802	1·0000	De la Rive & Marcet, Dulong.
	0·2884	1·0805	1·0340	De la Roche & Bérard.
Carbonic acid gas		0·6557	1·0000	Haykraft.
	0·2124	0·6925	1·0655	Suermann.

* This number cannot be right; for 1·0293 . 0·9757 = 1·0043.

	Specific Heat.		Relative Heat.	
	that of water = 1	that of air = 1	that of air = 1	
Carbonic acid gas			1·1750	Dulong.
		0·7838	1·1950	Apjohn.
			1·2220	De la Rive & Marcet.
	0·2210	0·8280	1·2583	De la Roche & Bérard.
		0·9835	1·5000	Clement & Desormes.
Sulphurous acid gas ..		0·4507	1·0000	De la Rive & Marcet.
Sulphuretted hydrogen		0·8485	1·0000	,, ,,
Hydrochor. acid gas ..		0·7925	1·0000	,, ,,
Nitrous oxide gas		0·6557	1·0000	,, ,,
	0·2240	0·7354	1·1229	Suermann.
			1·1600	Dulong.
		0·7827	1·1930	Apjohn.
	0·2369	0·8878	1·3503	De la Roche & Bérard.
Nitric oxide gas		0·9616	1·7000	De la Rive & Marcet.
Ammoniacal gas		1·6968	1·0000	,, ,,
Cyanogen gas		0·5547	1·0000	,, ,,
Olefiant gas.....			1·0660	Haykraft.
			1·5310	Dulong.
	0·4207	1·5763	1·5530	De la Roche & Bérard.
			1·5309	De la Rive & Marcet.

All gases, according to Haykraft, and all simple gases at least, according to De la Rive & Marcet, have the same relative heat: the greater relative heat which Haykraft found in olefiant gas he attributes to the mixture of ether vapour with the gas. But according to all other observations, this view first promulgated (*Gilb.* 45, 321) but afterwards retracted (*Gilb.* 48, 392) by Gay-Lussac, is very doubtful.

If the quantity of heat required to raise by 1° the temperature of air enclosed in a vessel with rigid sides be assumed = 1·000, the quantity required to produce the same rise of temperature in an equal quantity of air confined under the same pressure, in such a manner that while the pressure remains constant it can expand freely when heated, will be 1·421; and if it be again reduced by pressure to its former bulk, this quantity 1·421 of heat corresponding to the increase of volume must be set free. A distinction must therefore be made between (*a*) Relative Heat under constant volume, and (*b*) Relative Heat under constant pressure (Dulong). [The relative heats given in the table refer to *b*.] Air, oxygen, hydrogen, and carbonic oxide gas have the same relative heat under constant pressure; hence it may be surmised that they have likewise the same relative heat under constant volume, and therefore that they evolve the same quantity of heat when subjected to the same pressure. Carbonic acid gas under the same pressure shows a rise of temperature of only 0·337°, nitrous oxide gas of 0·343°, and olefiant gas of 0·240°. If it be assumed that all gases when equally compressed evolve the same quantity of heat, these last three gases must be supposed to have greater relative heat with reference to a given volume; and this may be reckoned (assuming that of air = 1) for carbonic acid gas, $0{\cdot}337 : 0{\cdot}421 = 1 : x = 1{\cdot}249$; for nitrous oxide gas = 1·227, and for olefiant gas = 1·754. To find the relative heat of carbonic acid gas with reference to a constant pressure, we have the proportion, $1{\cdot}421 : 1{\cdot}249 + 0{\cdot}421 = 1 : x = 1{\cdot}175$; and so on. According to these suppositions, all gases under the same pressure,

and when equally compressed under the same volume, evolve equal quantities of heat; and the rise of temperature thereby produced varies inversely as the relative heat of the gas referred to a constant volume.

If the relative heat of common air at 0·7405 metre external pressure be equal to 1, the relative heat of air under a pressure of 1·0058 met. (the density of which will be to that of the former = 1·3583 : 1) will be 1·2369, according to Delaroche & Bérard,—while the specific heat of this condensed air will, according to these numbers, be $\frac{1{\cdot}2369}{1{\cdot}3583} = 0{\cdot}9126$, the specific heat of air at the ordinary pressure being supposed = 1. If the relative heat of air under a pressure of 0·758 met. be assumed = 1, that of air at a pressure of 0·379 met. will, according to Clement & Desormes, be 0·693; at 0·189 met. it will be 0·540, and at 0·095 met., 0·368.

If the specific heat of air at − 20° = 1, that of air at + 52° will be 1·206; hence the specific heat of gases increases with the temperature (Gay-Lussac, *Ann. Chim.* 83, 108. *Comp.* Suermann, *Ann. Chim. Phys.* 63, 327.)

In the two tables which follow (pp. 241, 244) Av. denotes Avogadro,—C. D. Clement and Desormes,—Cf. Crawford,—Dl. Dalton,—Dz. Despretz,—D. M. De la Rive & Marcet,—Hs. Hess,—Kw. Kirwan,—Hm. Hermann,—Nm. Neumann,—P. D. Petit & Dulong,—Pr. Potter,—Rg. Regnault.

Specific Heat of Liquid and Solid Elementary Bodies that of Water = 1·0000.

Diamond.....	0·1192	D M	Molybdenum ..	0·0659	D M	Lead.....	0·0314	Rg
	0·1469	Rg		0·0722	Rg		0·0320	Pr
Graphite, nat...	0·2019	,,	Uranium	0·0619	,,		0·0400	Dl
— art.....	0·1970	,,	Manganese containing C	0·1441	,,	Iron.....	0·1054	Hm
Coke[1]	0·2036	,,	Arsenic	0·0804	Hm		0·1100	P D
—[2]	0·2017	,,		0·0810	Av		0·1130	Pr
—[3]	0·2031	,,		0·0814	Rg		0·1138	Rg
Charcoal strongly ignited....	0·2415	,,	Antimony.....	0·0470	Nm		0·1300	Dl
	0·2009	D M		0·0496	Hm	Cobalt	0·1070	Rg
— moderately heated.....	0·2964	,,		0·0508	Rg	— containing C	0·1171	,,
Charcoal from sugar	0·1592	,,	Tellurium	0·0515	Rg		0·1172	D M
— from oil of turpentine[4] ..	0·1801	,,		0·0520	Pr		0·1498	P D
Lamp-black....	0·2570	Av		0·0912	P D	Nickel	0·1035	,,
Animal charcoal	0·2608	Rg	Bismuth	0·0270	Nm		0·1086	Rg
Phosphorus....	0·1887	,,		0·0288	P D	— containing C	0·1163	,,
	0·2900	Hm		0·0308	Rg	Copper.....	0·0949	P D
	0·3850	Av		0·0330	Pr		0·0950	D M
Sulphur	0·1880	P D	Zinc.....	0·0927	P D		0·0951	Rg
	0·1900	Dl		0·0929	Nm		0·0960	Pr
	0·2026	Rg		0·0940	Pr		0·0961	Hm
	0·2090	Nm		0·0955	Rg	Mercury	0·0318	D M
Selenium.....	0·0675	Hm		0·1000	Dl		0·0330	Kw, Pr
	0·0834	D M	Cadmium.....	0·0385	Hm		0·0333	Rg
	0·0837	Rg		0·0567	Rg	Silver	0·0557	P D
Iodine	0·0541	,,		0·0576	D M		0·0570	Rg
	0·0890	Av	Tin	0·0514	,,		0·0590	Pr
Bromine	5·1350	D M		0·0515	P D	Gold.....	0·0298	P D
Tungsten.....	0·0350	,,		0·0560	Pr		0·0324	Rg
	0·0364	Rg		0·0562	Rg		0·0340	Pr
			Lead.....	0·0293	P D	Platinum.....	0·0314	P D
				0·0299	Hm	Palladium	0·0324	Rg
						Iridium	0·0593	,,
							0·0368	,,

[1] From gas-retorts. [2] From Anthracite from Wales containing 3 per cent. of ash.
[3] From cannel coal containing 4—5 per cent. ash. [4] Passed through a red-hot tube.

The capacity for heat of any given body increases with its temperature. If the specific heat of the following substances be determined, first by heating them to 100°, then plunging them into cold water and observing the temperature of the water,—secondly, by heating them to 300°, and repeating the same process, the following differences of specific heat will be found.

Heated to	Iron.	Mercury.	Zinc.	Antimony.	Silver.	Copper.	Platinum.	Glass.
100°	0·1098	0·033	0·0927	0·0507	0·0557	0·0949	0·0335	0·177
300°	0·1218	0·035	0·1015	0·0549	0·0611	0·1013	0·0355	0·190

Those metals whose rate of expansion increases most rapidly when they are heated, likewise increase most in specific heat; the relative heat also increases in so far as when the expansion amounts to $\frac{1}{100}$, the increased capacity for heat is about $\frac{1}{10}$. (Dulong and Petit.)

The specific heat of copper is reduced by violent hammering from 0·095 to 0·0935, but raised again by ignition to 0·0949: lead and tin, on the contrary, which do not increase in specific gravity under the die, likewise suffer no diminution of specific heat by pressure. (Regnault.)

¶ Regnault also finds that soft steel, the density of which at 14° C. is 7·8609, has a specific heat of 0·1165; hard steel of density 7·7982 has a specific heat of 0·1175.—The specific heat of soft bell-metal (80 Cu + 20 Sn), which has a density of 8·6843, is 0·0862, while the same metal hardened, in which state its density is 8·5797, has a specific heat of 0·0858. (*Pogg.* 62, 50.)

In the same memoir Regnault gives the specific heats of several metals in the finely divided state, as determined by the method of cooling. The following are the results.

Substances.	Specific Heat determined by cooling from:		
	20° to 15°.	15° to 10°.	10° to 5°.
Antimony	0·06424	0·06367	0·06305
Grain tin	0·05504	0·05546	0·05477
Banka tin (filings)	0·05662	0·05614	0·05651
Zinc	0·09123	0·09252	0·09142
Cadmium	0·05938	0·05969	0·05908
Bismuth	0·03639	0·03728	0·03732
Arsenic	0·09019	0·09085	0·09006
Copper	0·08847	0·08913	0·08842
Spongy platinum	0·03509	0·03449	0·03509
Silver filings	0·05424	0·05458	0·05433
,, ,,	0·05620	0·05612	0·05611
Precipitated silver:			
1. Very little pressed	0·08535	0·08441	0·08519
2. More strongly	0·05844	0·05772	0·05781
3. ,,	0·05749	0·05713	0·05749
4. ,,	0·05609	0·05601	0·05666
5. ,,	0·05777	0·05767	0·05793
6. ,,	0·06069	0·06038	0·06093
7. Strongly hammered and then rubbed	0·05634	0·05671	0 05654
8. More strongly	0·05616	0·05624	0·05650

¶

The greater the atomic weight of any substance the smaller will be the number of atoms of it required to make up a given absolute weight.

Since, for example, an atom of hydrogen weighs 1, an atom of sulphur 16, and an atom of silver 108, a pound of sulphur must contain $\frac{1}{16}$ and a pound of silver $\frac{1}{108}$ as many atoms as a pound of hydrogen. If then the specific heat (capacity for heat referred to a given weight) of any substance be multiplied into its atomic weight, the product will give the capacity for heat referred to a given number of atoms. This has been done in the following table, in which the data employed are those of De la Roche & Bérard, Regnault, Neumann, and De la Rive & Marcet, as given in the tables (pp. 239 and 241).

Capacity for Heat of the Atoms of Elementary Substances.

Substance.	Specific Heat.	Atomic Weight.	Product.	Substance.	Specific Heat.	Atomic Weight.	Product.
Oxygen gas ..	0·2361	8	1·8888	Antimony ..	0·0508	129	6·5532
Hydrogen gas	3·2936	1	3·2936	Tellurium ..	0·0515	64	3·2960
Nitrogen gas .	0·2754	14	3·8556	Bismuth	0·0308	106·4	3·2771
Diamond	0·1469	6	0·8814	Zinc	0·0955	32·2	3·0751
Graphite	0·2019	6	1·2114	Cadmium ..	0·0567	55·8	3·1639
Charcoal	0·2009	6	1·2054	Tin	0·0562	59	3·3158
"	0·2415	6	1·4490	Lead	0·0314	103·8	3·2593
"	0·2964	6	1·7784	Iron	0·1138	27·2	3·0954
Phosphorus ..	0·1887	31·4	5·9250	Cobalt.....	0·1070	29·6	3·1672
Sulphur	0·2026	16	3·2416	Nickel.....	0·1086	29·6	3·2146
Selenium	0·0837	40	3·3480	Copper	0·0951	31·8	3·0242
Iodine	0·0541	126	6·8166	Mercury	0·0333	101·4	3·3766
Bromine	0·1350	78·4	10·5840	Silver	0·0570	108·1	6·1617
Tungsten	0·0364	95	3·4580	Gold	0·0324	199	6·4476
Molybdenum	0·0722	48	3·4656	Platinum ..	0·0324	98·7	3·1979
Manganese ..	0·1441	27·6	3·9772	Palladium ..	0·0593	53·4	3·1666
Arsenic	0·0814	75·2	6·1213	Iridium	0·0368	98·7	3·6322

From their exact determinations of the specific heats of several elementary bodies, Petit & Dulong deduced the law, that the specific heats of these bodies vary inversely as their atomic weights,—so that an atom of any simple substance, whether its volume be great or small, has the same capacity for heat, and requires the same quantity of heat to raise its temperature through a given number of degrees, as an atom of any other elementary substance. The exceptions which they found to this rule have been for the most part removed by the later observations of Regnault, as given in the preceding table. In most substances, the product of the specific heat into the atomic weight is nearly 3·2. Exact agreement is not to be expected, inasmuch as the specific heat of a body varies with its density, and undoubtedly increases to a great degree when the body passes from the solid to the liquid or gaseous state.

With regard to the non-gaseous substances of the foregoing table, the following circumstances may be noticed. The deviation in the case of manganese perhaps arises from the presence of carbon in the metal examined by Regnault, and that in the case of iridium from the impurity of the metal.—Phosphorus, iodine, arsenic, antimony, silver, and gold, exhibit twice as much capacity for heat in the same number of atoms as most other substances. This exception might be made to disappear by halving, as is done by many chemists, the atomic weights of these substances. But if the atomic weight of iodine be reduced one half, the same must necessarily be done with regard to hydrogen and nitrogen, and then the

specific heat of these bodies would also be reduced one half. this halving would render the chemical formulæ unnecessaril

The capacity for heat of liquid bromine appears to be three tin as that of most elements; but from the analogy between this and iodine, it may be supposed that the capacity of solid brom twice as great as that of the majority of simple substances. Th for heat of carbon in the form of diamond is $\frac{1}{4}$, in that of grap in that of charcoal about $\frac{1}{2}$ the ordinary amount. These exce not be explained away; we cannot treble or quadruple, nor e the atomic weight of carbon without incurring great inconvenie

Among gaseous bodies, nitrogen conforms most closely to t the larger product which it gives is referable to the increase heat arising from the gaseous form. Hydrogen, whose specif probably estimated too low by De la Roche & Bérard, is a formity with the law. The atoms of oxygen, on the contrary have only half the ordinary capacity for heat.—If we suppose, kraft, De la Rive, and others, that all simple gases have the sa heat, and that the law of Dulong & Petit holds good without e the law of Berzelius (p. 45) will be established, according to elementary gases all contain the same number of atoms in volume; and the division (p. 53) of gases into 6, 2, and 1-aton considered as incorrect. But the preceding table shows that to the law of Dulong & Petit occur even among gases. In merely compare oxygen and hydrogen with one another, n atomic weight of hydrogen = 1, and that of oxygen = 16, t for heat of the atom of hydrogen will be 3·2936 . 1 = 3·2396, the atom of oxygen 0·2361 . 16 = 3·7776,—products which a pretty closely to those of other substances. But if the atomi oxygen be made = 16, that of sulphur must be increased to 32 of the metals must also be doubled, and then their product v 3·2, but 6·4; or if the atomic weight of sulphur be made = 16, = 8, and of hydrogen = 0·5, the last two bodies will give or half the product given by sulphur.

All this being considered, it is impossible to get rid of all tions to the law of Dulong & Petit; and since this law is not applicable, it would be useless to remove a few only of the exc altering the atomic weights, particularly when such alterati entail unnecessary complexity on chemical formulæ. But th tions bear a simple relation to the general law. Thus, if the c heat of an atom of sulphur, and of most other substances, be ass that of an atom of diamond will be = $\frac{1}{4}$, of oxygen = $\frac{1}{2}$, iodine, phosphorus, arsenic, antimony, silver, and gold = 2.

Specific Heat of Liquid and Solid Compounds, that of Water =

Cu^2O, natural	0·1073	Nm	G O	0·2
H O, ice.....	0·7200	C D	U O	0·0
	0·9000	Kw		0·1
	0·9200	Av	Mn O.....	0·1
Ca O	0·1790	Av	Zn O	0·1
	0·3000	Dl		0·1
Mg O.....	0·1696	Hm		0·1
	0·2439	Rg		0·1
	0·2760	Nm		0·1
Y O	0·1347	Hm	Sn O	0·0

$Pb\,O$	0·0500	Av	$Hg^2\,Cl$	0·0410	Av
—— fused	0·0509	Rg		0·0495	Hm
—— powdered	0·0512	,,		0·0520	Rg
	0·0544	Hm	$K\,Cl$	0·1403	Hm
$Ni\,O$	0·1623	Rg		0·1840	Av
—— heated to whiteness	0·1588	,,	—— fused	0·1729	Rg
	0·1370	Nm	$Na\,Cl$	0·2210	Av
$Cu\,O$	0·1420	Rg		0·2300	Dl
	0·1460	Av	—— fused	0·2140	Rg
	0·227	Cf	—— Rock-salt	0·1817	Hm
$Hg\,O$	0·0490	Nm	$L\,Cl$	0·2650	,,
	0·0500	Av	$Ba\,Cl$	0·0780	,,
	0·0318	Rg	—— fused	0·0896	Rg
$Mn^3\,O^4$	0·1651	Hm	$Sr\,Cl$	0·0972	Hm
$Pb^3\,O^4$	0·0611	Nm	—— fused	0·1199	Rg
	0·0650	Av	$Ca\,Cl$	0·1102	Hm
$Fe^3\,O^4$, natural	0·1611	Nm		0·1940	Av
	0·1678	Rg	—— fused	0·1642	Rg
$Ce^2\,O^3$	0·0984	Hm	$Mg\,Cl$, fused	0·1946	,,
$Al^2\,O^3$, artificial	0·1963	,,	$Mn\,Cl$	0·1425	,,
	0·2000	Av	$Zn\,Cl$	0·1362	,,
— Corundum	0·1942	Nm	$Sn\,Cl$	0·1016	,,
	0·1976	Rg	$Pb\,Cl$	0·0664	,,
— Sapphire	0·1972	Nm	$Hg\,Cl$	0·0689	,,
	0·2173	Rg		0·0690	Av
$Cr^2\,O^3$	0·1796	,,		0·0715	Hm
	0·1960	Nm	$Ag\,Cl$	0·0844	,,
	0·2126	Hm	—— fused	0·0911	Rg
$Bi^2\,O^3$	0·0605	Rg	$Ti\,Cl^2$	0·1914	,,
$Fe^2\,O^3$, artificial	0·1757	,,	$Sn\,Cl^2$	0·1476	,,
—— strongly ignited	0·1681	,,	$P\,Cl^3$	0·2092	,,
$Fe^2\,O^3$, Eisen-glanz	0·1669	Rg	$As\,Cl^3$	0·1760	,,
	0·1692	Nm	$K\,Br$, fused	0·1132	,,
$Si\,O^2$, Quartz	0·1719	Hm	$Na\,Br$,,	0·1384	,,
	0·1790	Av	$Pb\,Br$,,	0·0533	,,
	1·1883	Nm	$Ag\,Br$,,	0·0739	,,
	0·1913	Rg	$Cu^2\,I$,,	0·0687	,,
$Ti\,O^2$, artificial	0·1716	,,	$Hg^2\,I$	0·0395	,,
— Rutile	0·1630	Hm	$K\,I$	0·0657	Hm
	0·1703	Rg	—— fused	0·0819	Rg
	0·1724	Nm	$Na\,I$,,	0·0868	,,
$Sn\,O^2$, artificial	0·0933	Rg	$Pb\,I$,,	0·0427	,,
	0·1110	Av	$Hg\,I$,,	0·0420	,,
— Tinstone	0·0900	Hm	$Ag\,I$,,	0·0616	,,
	0·0931	Nm	$Cu^2\,S$, fused	0·1212	,,
$Mn\,O^2$	0·1910	Av	$Zn\,S$, zinc-blende	0·1145	Nm
$B\,O^3$, vitrified	0·2374	Rg		0·1230	Rg
$W\,O^3$	0·0722	Hm	$Sn\,S$, fused	0·0836	,,
	0·0798	Rg	$Pb\,S$, Galena	0·0460	Av
$Mo\,O^3$	0·1324	,,		0·0509	Rg
$As\,O^3$	0·1279	,,		0·0527	Hm
	0·1319	Hm		0·0530	Nm
	0·1410	Av	$Fe\,S$, fused	0·1357	Rg
— vitreous	0·1309	D M	$Co\,S$,,	0·1251	,,
— opaque	0·1320	,,	$Ni\,S$,,	0·1281	,,
$Sb\,O^3$	0·0901	Rg	$Hg\,S$, Vermillion	0·0480	Av
$Sb\,O^4$	4·0953	,,		0·0512	Rg
	0·1300	Nm		0·0520	Nm
$Na\,F$	0·2678	Hm		0·0528	Hm
$Ca\,F$, Fluorspar	0·1912	,,		0·0597	D M
	0·2082	Nm	$Ag\,S$, fused	0·0746	Rg
—— ignited	0·2149	Rg	$Fe\,Cu\,S^2$, Copper Pyrites	0·1289	Nm
$Cu\,Cl$	0·1383	,,	$Fe^7\,S^8$, Magnetical Pyrites	0·1533	,,

$Fe^2 S^3$, Magnetical Pyrites	0·1602	Rg	Mg O, C O^2, natural ..	0·2220	Nm
$Bi^2 S^3$	0·0600	,,	Ca O, CO^2 + Mg O,		
C S^2	0·1969	Hm	C O^2, Bitter spar	0·2179	,,
	0·3290	D M	—— Dolomite	0·2174	Rg
Mo S^2, natural	0·1097	,,	Pb O, C O^2, artificial ..	0·0860	,,
	0·1067	Nm	—— Lead spar.....	0·0814	Nm
	0·1233	Rg		0·0818	Hm
As S^2	0·1111	Nm	Fe O, C O^2, natural	0·1820	Nm
Sn S^2, Mosaic gold	0·1193	Rg		0·1934	Rg
Fe S^2, Iron Pyrites	0·1275	Nm	Chrysolite	0·2056	Nm
	0·1301	Rg	Zircon	0·1456	Rg
	0·1350	Av	Topaz.....	0·2018	Nm
	0·1396	D M	Zoisite	0·1940	,,
—— White Iron Pyrites	0·1332	Nm	Augite	0·1937	,,
As S^3, natural	0·1050	Av	Diopside	0·1906	,,
	0·1132	Nm	Basaltic Hornblende	0·1976	,,
	0·1244	Hm	Actynolite.....	0·2046	,,
Sb S^3	0·0840	Rg	Tremolite	0·2070	,,
—— natural.....	0·0907	Nm	Adularia.....	0·1861	,,
	0·0995	Hm	Ordinary Felspar	0·1911	,,
	0·1286	Rm	Albite.....	0·1961	Nm
Fe^2 As S^2, natural	0·1012	Nm	Labrador	0·1926	,,
Co As S^2 ,, ...	0·1070	,,	Glass.....	0·1977	Rg
Co As.....	0·0920	,,	Flint-glass.....	0·1900	Dl
Steel, hard.....	0·1024	Pr	Iserine	0·1762	Nm
—— soft	0·1080	,,	K O, B O^3, fused	0·2049	Rg
Steel	0·1185	Rg	Na O, B O^3 ,, ...	0·2571	,,
Cast iron, white.....	0·1298	,,	Pb O, B O^3 ,, ...	0·0905	,,
Fine metal.....	0·1273	,,	K O, 2B O^3 ,, ...	0·2197	,,
Brass.....	0·0939	,,	Na O, 2B O^3 ,, ...	0·2382	,,
Sn Bi.....	0·0400	,,	Pb O, 2B O^3 ,, ...	0·1141	,,
Sn^2 Bi	0·0450	,,	K O, Cr O^3	0·1850	,,
Sn^4 Bi^2 Sb	0·0461	,,	K O, 2Cr O^3	0·1894	,,
Pb Sb^2	0·0388	,,	H O, S O^3	0·3490	D M
Pb Sn.....	0·0407	,,		0·3500	Dl
Pb Sn^2	0·0451	,,	K O, S O^2.....	0·1690	Av
Pb Sn^2 Bi	0·0448	,,	—— fused.....	0·1901	Rg
Pb Sn^2 Bi^2	0·0608	,,	Na O, S O^3	0·2311	,,
Hg Sn	0·0729	,,	—— dry	0·2630	Av
Hg Sn^2	0·0659	,,	Ba O, S O^3, natural	0·1088	Nm
Hg Pb	0·0383	,,		0·1128	Rg
K O, H O	0·3580	Av	Sr O, S O^3, natural	0·1356	Nm
Ca O, H O	0·3000	,,	—— artificial	0·1428	Rg
	0·4000	Dl	Ca O, S O^3, natural	0·1854	Nm
Al^2 O^3, 3H O	0·4200	Av	—— ignited	0·1900	Av
Fe^2 O^3, 3HO.....	0·1880	,,		0·1966	Rg
K O, C O^2, dry.....	0·2370	,,	Mg O, S O^3, ignited....	0·2216	,,
—— fused.....	0·2162	Rg	Pb O, S O^3	0·0872	,,
Na O, C O^2, dry	0·3060	Av	—— natural.....	0·0848	Nm
—— fused.....	0·2727	Rg	Zn O, S O^3, dry	0·2130	Av
Ba O, C O^2, natural	0·1078	Nm	Fe O, S O^3 ,, ...	0·1450	,,
	0·1104	Rg	Cu O, S O^3 ,, ...	0·1800	,,
Sr O, C O^2, natural	0·1445	Nm	Apatite	0·1787	Hm
—— artificial	0·1448	Rg	3Pb O, P O^5, fused	0·0798	Rg
Ca O, C O^2, artificial....	0·2030	Av	2K O, P O^5, ,, ...	0·1910	,,
	0·2700	Dl	2Na O, P O^5 ,, ...	0·2283	,,
—— Iceland spar.....	0·2086	Rg	2Pb O, P O^5 ,, ...	0·0821	,,
—— Calcspar	0·1945	Hm	Ca O, P O^5 ,, ...	0·1992	,,
	0·2046	Nm	3Pb O, As O^5 ,, ...	0·0728	,,
—— statuary marble ..	0·2158	Rg	Ca O, As O^5 ,, ...	0·1563	,,
—— chalk.....	0·2148	,,	K O, Cl O^5 ,, ...	0·2096	,,
—— Arragonite	0·2018	Nm	K O, N O^5.....	0·2690	Av
	0·2085	Rg	—— fused..	0·2387	Rg

$Na\,O, NO^5$	0·2400	Av	Solution of ammonia, sp. gr. 0·948	0·0300	Dl
—— fused	0·2782	Rg	Alcohol	0·6220	Dz
$Ba\,O, NO^5$	0·1334	Hm	Alcohol	0·6320	D M
	0·1523	Rg	Ether	0·5200	Dz
$Sr\,O, NO^5$	0·1683	Hm		0·5500	D M
$Ag\,O, NO^5$, fused	0·1435	Rg	Volatile oil from oil-gas*	0·4750	
$Ca\,O, SO^3, 2H\,O$	0·2728	Nm	Rock-oil	0·4930	
	0·3020	Av	Oil of turpentine	0·4248	Rg
Aqueous Hydrochloric acid sp. gr. 1·153	0·6000	Dl		0·4620	Dz
$H\,O, NO^5$	0·4450	Hs		0·4720	Kw
$2H\,O, NO^5$	0·5100	,,		0·4880	D M
Aqueous Nitric acid, sp. gr. 1·36	0·6300	Dl	Olive oil	0·5040	
Aqueous Nitric acid, sp. gr. 1·2	0·7600	,,	Whale-oil	0·5200	

The specific heat of a compound is diminished by increasing its density; thus, peroxide of iron and protoxide of nickel have their specific heat diminished by strong ignition. (Regnault.)—Dimorphism appears to exert no great influence upon specific heat; *e. g.*, in calcspar and arragonite; in common and white iron pyrites. (Neumann.)—The specific heat of water at 0° is to its specific heat at 100° as 1·000 : 1·0176. (Neumann.)

¶ Regnault in the memoir before referred to (*Pogg.* 62, 50) also gives the specific heats of the following liquids, determined by the method of cooling:

Liquids.	Mean Densities.			Specific Heats.		
	20°....15°	15°....10°	10°....5°	20°....15°	15°....10°	15°....5°
Mercury	13·538	13·570	13·582	0·0290	0·0283	0·0282
Terebene	0·8564	0·8605	0·8645	0·4267	0·4156	0·4154
Oil of lemons	0·8518	0·8558	0·8597	0·4501	0·4424	0·4489
Petrolene	0·8888	0·8921	0·8953	0·4342	0·4325	0·4321
Benzin	0·8838	0·8887	0·8931	0·3932	0·3865	0·3999
Nitro-benzid	1·2054	1·2107	1·2159	0·3449	0·3478	0·3524
Chloride of silicon	1·4884	1·4983	1·5083	0·1904	0·1904	0·1914
Bichloride of titanium	1·7322	1·7403	1·7487	0·1828	0·1802	0·1810
,, tin	2·2368	2·2492	2·2618	0·1416	0·1402	0·1421
Terchloride of phosphorus	1·5911	1·6001	1·6091	0·1991	0·1987	0·2017
Sulphuret of carbon	1·2676	1·2750	1·2823	0·2206	0·2183	0·2179
Ether	0·7185	0·7241	1·7297	0·5157	0·5158	0·5207
Hydrosulphuric ether	0·8356	0·8406	0·8456	0·4772	0·4656	0·4715
Hydriodic ether	1·9348	1·9457	1·9567	0·1584	9·1584	0·1587
Alcohol	0·8072	0·8113	0·8150	0·6148	0·6017	0·5987
Oxalic ether	1·0898	1·0953	1·1010	0·4554	0·4521	0·4629
Wood-spirit	0·8130	0·8173	0·8217	0·6009	0·5868	0·5901
Hydrobromic ether	1·4582	1·4679	1·4775	0·2153	0·2135	0·2164
Chloride of sulphur	1·6793	1·6882	1·6970	0·2038	0·2024	0·2048
Acetic acid (glacial)	1·0535	1·0591	1·0647	0·4618	0·4599	0·4587

Regnault likewise gives the mean specific heats of the following isomeric liquids for temperatures between 100° and 15° C.

* The most volatile of the oils which Faraday obtained from oil-gas.

$Fe^7 S^8$, Magnetical Pyrites	0·1602	Rg	Mg O, C O^2,
$Bi^2 S^3$	0·0600	,,	Ca O, C O^2
C S^2	0·1969	Hm	C O^2, Bitte
	0·3290	D M	—— Dolomi
Mo S^2, natural	0·1097	,,	Pb O, C O^2,
	0·1067	Nm	—— Lead sp
	0·1233	Rg	
As S^2	0·1111	Nm	Fe O, C O^2,
Sn S^2, Mosaic gold	0·1193	Rg	
Fe S^2, Iron Pyrites	0·1275	Nm	Chrysolite ...
	0·1301	Rg	Zircon .....
	0·1350	Av	Topaz.....
	0·1396	D M	Zoisite .....
—— White Iron Pyrites	0·1332	Nm	Augite .....
As S^3, natural	0·1050	Av	Diopside ..
	0·1132	Nm	Basaltic Ho
	0·1244	Hm	Actynolite .
Sb S^3	0·0840	Rg	Tremolite ..
—— natural.....	0·0907	Nm	Adularia...
	0·0995	Hm	Ordinary Fe
	0·1286	Rm	Albite.....
Fe^2 As S^2, natural.....	0·1012	Nm	Labrador ..
Co As S^2 ,, ...	0·1070	,,	Glass .....
Co As.....	0·0920	,,	Flint-glass
Steel, hard.....	0·1024	Pr	Iserine ...
—— soft	0·1080	,,	K O, B O^3,
Steel	0·1185	Rg	Na O, B O^3
Cast iron, white.....	0·1298	,,	Pb O, B O^3
Fine metal.....	0·1273	,,	K O, 2B O^3
Brass	0·0939	,,	Na O, 2B O^3
Sn Bi.....	0·0400	,,	Pb O, 2B O^3
Sn^3 Bi	0·0450	,,	K O, Cr O^3
Sn^4 Bi^2 Sb	0·0461	,,	K O, 2Cr O^3
Pb Sb^2	0·0388	,,	H O, S O^3
Pb Sn.....	0·0407	,,	
Pb Sn^2	0·0451	,,	K O, S O^3,
Pb Sn^2 Bi	0·0448	,,	—— fused.
Pb Sn^2 Bi^2	0·0608	,,	Na O, S O^3
Hg Sn	0·0729	,,	—— dry
Hg Sn^2	0·0659	,,	Ba O, S O^3,
Hg Pb	0·0383	,,	
K O, H O	0·3580	Av	Sr O, S O^3,
Ca O, H O	0·3000	,,	—— artificia
	0·4000	Dl	Ca O, S O^3,
Al^2 O^3, 3H O	0·4200	Av	—— ignited
Fe^2 O^3, 3HO.....	0·1880	,,	
K O, C O^2, dry.....	0·2370	,,	Mg O, S O^3,
—— fused.....	0·2162	Rg	Pb O, S O^3
Na O, C O^2, dry	0·3060	Av	—— natural
—— fused.....	0·2727	Rg	Zn O, S O^3,
Ba O, C O^2, natural	0·1078	Nm	Fe O, S O^3
	0·1104	Rg	Cu O, S O^3
Sr O, C O^2, natural	0·1445	Nm	Apatite ....
—— artificial	0·1448	Rg	3Pb O, P O^5,
Ca O, C O^2, artificial....	0·2030	Av	2K O, P O^5,
	0·2700	Dl	2Na O, P O^5
—— Iceland spar.....	0·2086	Rg	2Pb O, P O^5
—— Calcspar	0·1945	Hm	Ca O, P O^5
	0·2046	Nm	3Pb O, As
—— statuary marble ..	0·2158	Rg	Ca O, As
—— chalk.....	0·2148	,,	K O, Cl O
—— Arragonite	0·2018	Nm	K O, N O
	0·2085	Rg	—— fuse

...stance.	Specific Heat.	Atomic Weight.	Product.
..., SiO^2 ..	0·1456	91·6	13·337
..., BO^3	0·2049	82	16·802
..., BO^3 ...	0·2571	66	16·969
..., BO^3 ...	0·0905	146·6	13·267
..., $2BO^3$ ...	0·2197	116·8	25·661
..., $2BO^3$ ..	0·2382	100·8	24·010
..., $2BO^3$ ..	0·1141	181·4	20·698
..., CrO^3 ...	0·1860	99·3	18·370
..., $2CrO^3$ ..	0·1894	151·4	28·675
..., SO^2	0·3490	49	17·101
..., SO^3	0·1901	87·2	16·576
..., SO^3....	0·2311	71·2	16·454
..., SO^3....	0·1128	116·6	13·152
..., SO^3	0·1428	92	13·138
..., SO^3....	0·1854	68·5	12·700
..., SO^3 ...	0·2216	60·7	13·451
..., SO^3....	0·0848	151·8	12·873
..., PO^5...	0·0798	406·8	32·463
..., PO^5 ...	0·1910	165·8	31·668
..., PO^5...	0·2283	133·8	30·546
..., PO^5...	0·0821	295	24·219
..., PO^5....	0·1992	99·9	19·900
..., AsO^5..	0·0728	450·6	32·804
..., AsO^5 ...	0·1563	162·4	25·383
..., ClO^5....	0·2096	122·6	25·697
..., NO^5	0·2387	101·2	24·156
..., NO^5 ...	0·2782	85·2	23·703
..., NO^5 ...	0·1435	170·1	24·109
..., NO^5 ...	0·1523	130·6	19·890
..., NO^5....	0·1683	106	17·840
$CaO, SO^3, 2HO$	0·2728	86·5	23·597

...of similar stoichiometrical composi-
...., metallic oxides and sulphurets,—
...cid; and Regnault showed that the
many other series of compounds.
...llic sulphurets, the heat-capacity of
...y taking the sum of the capacities
..., also L. Gmelin. (Gehler. *Physik.*
which this is based may, with a few
...y applicable in the following terms:
...ound atom is formed, retain therein
possess when separate; and conse-
...pound atom is the sum of the heat-
...compose it. Some cases however
...hat the heat-capacity of certain sub-
...n, varies by simple multiples accord-
...exist. Exact agreement is not to be
great differences between the results
...s only in the case of a few substances,
...ctly determined;—and moreover, the
...ries according to circumstances. It
...hat in all cases when the specific heat
...e liquid state, the heat-capacity of the
...hat which results from calculation,—un-
...he case of water, the passage of a body
... is attended with an increase of specific
...nation between the results of calculation
will be taken from the foregoing table and

Oil of turpentine	0·4672	Oil of lemons	0·4879
Terebene	0·4656	—— orange	0·4886
Terebilene.....	0·4580	Juniper oil	0·4776
Camphilene	0·4518	Petrolenè	0·4684

Favre and Silbermann (*Comptes rendus*, 23, 524) and Andrews (*Qu. J. of Chem. Soc.* 1, 27) have also determined the specific heats of a considerable number of liquids. The results obtained by these experimenters are given in the following table:

Liquid.	Sp. Heat.	Obs.	Liquid.	Sp. Heat.	Obs.
Bromine	0·107	A.	Acetic ether	0·48344	F. S.
Alcohol	0·64490	F. S.	,, ...	0·474	A.
,, ...	0·617	A.	Formic ether	0·485	,,
Wood spirit.....	0·67127	F. S.	Oxalic ether	0·457	,,
,, ...	0·613	A.	Butyrate of methyl ..	0·49176	F. S.
Fusel oil	0·58728	F. S.	Ethal	0·51600	,,
Ether	0·50342	,,	Oil of turpentine	0·46727	,,
,, ...	0·517	A.	Terebene	0·52409	,,
Amylic ether	0·52117	F. S.	Oil of lemons	0·50233	,,
Acetic acid	0·50822	,,			
Formic acid	0·60401	,,	Hydrocarbons:		
Valerianic acid.....	0·47857	,,	$C^{12}H^{12}$, B. P. 198°..	0·49385	,,
Butyric acid.....	0·41420	,,	$C^{15}H^{15}$, ,, 255°..	0·49680	,,

In the subjoined table, the specific heat, as far as it appears to have been correctly determined, is again compared with the atomic weight, and thus the capacity for heat of compound atoms is found.

Capacity for Heat of the Atoms of Compounds.

No.	Substance.	Specific Heat.	Atomic Weight.	Product.	No.	Substance.	Specific Heat.	Atomic Weight.	Product.
1	Cu^2O.....	0·1173	71·6	7·683	15	K Cl	0·1729	74·6	12·898
2	H O, ice.....	0·7200	9	6·480		Na Cl	0·2140	58·6	12·540
3	Mg O	0·2439	20·7	5·049		L Cl	0·2650	41·8	11·077
	Y O.....	0 1347	40·2	5·415		Ag Cl	0 0911	143·5	13·073
	Mn O.....	0·1570	35·6	5·589	16	Ba Cl	0·0896	104	9·318
	Zn O	0·1320	40·2	5·306		Sr Cl.....	0·1199	79·4	9·520
	Pb O.....	0·0509	111·8	5·691		Ca Cl	0·1642	55·9	9·179
	Ni O.....	0·1588	37·6	5·952		Mg Cl.....	0·1946	48·1	9·360
	Hg O	0·0518	109·4	5·667		Mn Cl	0·1425	63	8·977
4	Mn^2O^4	0·1651	114·8	18·952		Zn Cl.....	0·1362	67·6	9·207
	Pb^3O^4	0·0611	343·4	20·982		Sn Cl	0·1016	94·4	9·591
	Fe^3O^4	0·1641	113·6	19·062		Pb Cl	0·0664	139·2	9·243
5	Al^2O^3	0·2173	51·4	11·169		Hg Cl.....	0·0689	136·8	9·425
6	Cr^2O^3	0·1796	80·2	14·404	17	$Ti Cl^2$.....	0·1914	95·3	18·240
	Bi^2O^3	0·0605	236·8	14·326		$Sn Cl^2$.....	0·1476	129·8	19·158
	Fe^2O^3	0·1669	78·4	13·085	18	$P Cl^3$	0·2092	137·6	28·786
7	$Si O^2$.....	0·1913	30·8	5·892		$As Cl^3$	0·1760	181·4	31·926
	$Ti O^2$	0·1703	40·5	6·897	19	K Br.....	0·1132	117·6	13·312
	$Sn O^2$	0·0933	75	6·997		Na Br.....	0·1384	101·6	14·061
8	$Mn O^2$	0·1910	43·6	8·328		Ag Br.....	0·0739	186·5	13·782
9	$B O^3$.....	0·2374	34·8	8·261	20	Pb Br.....	0·0533	182·2	9·711
10	$W O^3$	0·0798	119	9·496	21	$Cu^2 I$	0·0687	189·6	13·025
	$Mo O^3$	0·1324	72	9·533		$Hg^2 I$	0·0395	328·8	12·987
11	$As O^3$	0·1279	115·2	14·734	22	K I	0·0819	165·2	13·530
	$Sb O^3$	0·0901	153	13·785		Na I	0·0868	149·2	12·950
12	$Sb O^4$	0·0953	161	15·343		Ag I	0·0616	234·1	14·420
13	Ca F.....	0·2082	39·2	8·164	23	Pb I	0·0427	229·8	9·812
14	$Cu^2 Cl$	0·1383	99	13·692		Hg I	0·0420	227·4	9·551
	$Hg^2 Cl$	0·0520	238·2	12·386	24	$Cu^2 S$	0·1212	79·6	9·647

No.	Substance.	Specific Heat.	Atomic Weight.	Product.	No.	Substance.	Specific Heat.	Atomic Weight.	Product.
25	ZnS	0·1230	48·2	5·929		$2ZrO, SiO^2$	0·1456	91·6	13·337
	SnS	0·0836	75	6·270	43	KO, BO^3	0·2049	82	16·802
	PbS	0·0509	119·8	6·098		NaO, BO^3	0·2571	66	16·969
	FeS	0·1357	43·2	5·862	44	PbO, BO^3	0·0905	146·6	13·267
	CoS	0·1251	45·6	5·704	45	$KO, 2BO^3$	0·2197	116·8	25·661
	NiS	0·1281	45·6	5·841		$NaO, 2BO^3$	0·2382	100·8	24·010
	HgS	0·0480	117·4	6·017	46	$PbO, 2BO^3$	0·1141	181·4	20·698
26	AgS	0·0746	124·4	9·258	47	KO, CrO^3	0·1850	99·3	18·370
27	Bi^2S^3	0·0600	260·8	15·648	48	$KO, 2CrO^3$	0·1894	151·4	28·675
28	CS^2	0·3290	38	12·502	49	HO, SO^3	0·3490	49	17·101
29	MoS^2	0·1233	80	9·864	50	KO, SO^3	0·1901	87·2	16·576
	SnS^2	0·1193	91	10·856		NaO, SO^3	0·2311	71·2	16·454
30	FeS^2	0·1301	59·2	7·702	51	BaO, SO^3	0·1128	116·6	13·152
31	AsS^2	0·1111	107·2	11·910		SrO, SO^3	0·1428	92	13·138
32	AsS^3	0·1132	123·2	13·946		CaO, SO^3	0·1854	68·5	12·700
33	SbS^3	0·0907	177	16·054		MgO, SO^3	0·2216	60·7	13·451
34	$CoAs$	0·0920	92	9·642		PbO, SO^3	0·0848	151·8	12·873
35	$SnBi$	0·0400	165·4	6·616	52	$3PbO, PO^5$	0·0798	406·8	32·463
36	Sn^2Bi	0·0450	224·4	10·098	53	$2KO, PO^5$	0·1910	165·8	31·668
37	Pb^2Sb	0·0388	336·6	13·060		$2NaO, PO^5$	0·2283	133·8	30·546
38	$PbSn$	0·0407	162·8	6·626	54	$2PbO, PO^5$	0·0821	295	24·219
39	$PbSn^2$	0·0451	221·8	10·003	55	CaO, PO^5	0·1992	99·9	19·900
40	$KO\ CO^2$	0·2162	69·2	14·961	56	$3PbO, AsO^5$	0·0728	450·6	32·804
	NaO, CO^2	0·2727	53·2	14·508	57	KO, AsO^5	0·1563	162·4	25·383
41	BaO, CO^2	0·1104	98·6	10·885		KO, ClO^5	0·2096	122·6	25·697
	SrO, CO^2	0·1448	74	10·715		KO, NO^5	0·2387	101·2	24·156
	CaO, CO^2	0·2086	50·5	10·534		NaO, NO^5	0·2782	85·2	23·703
	MgO, CO^2	0·2220	42·7	9·479		AgO, NO^5	0·1435	170·1	24·109
	PbO, CO^2	0·0814	133·8	10·891	58	BaO, NO^5	0·1523	130·6	19·890
	FeO, CO^2	0·1934	57·2	11·062		SrO, NO^5	0·1683	106	17·840
42	$2MgO, SiO^2$	0·2056	72·2	14·844	59	$CaO, SO^3, 2HO$	0·2728	86·5	23·597

Neumann first shewed that atoms of similar stoichiometrical composition have the same capacity for heat, *e. g.*, metallic oxides and sulphurets,—and salts of carbonic and sulphuric acid; and Regnault showed that the same law was further applicable to many other series of compounds. Hermann showed that in certain metallic sulphurets, the heat-capacity of the compound atom might be found by taking the sum of the capacities of the metal and of sulphur. [*Comp.* also L. Gmelin. (Gehler. *Physik. Wörterbuch.* 9, 141.)] The law upon which this is based may, with a few exceptions, be enunciated as generally applicable in the following terms: The simple atoms by which a compound atom is formed, retain therein the same capacity for heat that they possess when separate; and consequently, the heat-capacity of a compound atom is the sum of the heat-capacities of the simple atoms which compose it. Some cases however can only be explained by supposing that the heat-capacity of certain substances, especially carbon and oxygen, varies by simple multiples according to the compound in which they exist. Exact agreement is not to be expected, since—as is shown by the great differences between the results obtained by different observers—it is only in the case of a few substances, that the specific heat has been exactly determined;—and moreover, the specific heat of the same body varies according to circumstances. It must be especially borne in mind that in all cases when the specific heat of a compound is determined in the liquid state, the heat-capacity of the atom thus found is greater than that which results from calculation,—undoubtedly because, as shown in the case of water, the passage of a body from the solid to the liquid state is attended with an increase of specific heat. Since then an approximation between the results of calculation and experiment (which latter will be taken from the foregoing table and

annexed within brackets) is all that can be indicated, we may be allowed to shorten the numbers.

According to the table (p. 243) the atoms of most simple substances have the same capacity for heat, viz. 3·2;—let this be called the normal capacity.—Carbon in the form of diamond seems to have $\frac{1}{4}$ (0·8) and oxygen $\frac{1}{2}$ (1·6) of this normal capacity: on the contrary, chlorine, iodine, bromine, phosphorus, arsenic, antimony, silver and gold (and judging from the specific heats of their compounds, likewise, potassium, sodium, and lithium) have twice the normal capacity, viz. 6·4. In many compounds however, oxygen appears to enter with 2·4 or $\frac{3}{4}$ of the normal capacity, and in ice to possess the normal capacity itself: similarly, carbon, sulphur, and nitrogen appear to possess different capacities for heat, according to the nature of the compound in which they are formed.

1.*2Cu 6·4 + O 1·6 = 8·0 (7·68).
2. H 3·2 + O 3·2 = 6·4 (6·48).
3. Metal 3·2 + O 2·4 = 5·6 (5·52).
4. 3Metal 9·6 + 4O (at 2·4) 9·6 = 19·2 (19·66).
5. 2Al 6·4 + 3O (at 1·6) 4·8 = 11·2 (11·17).
6. 2Metal 6·4 + 3O (at 2·4) = 7·2 = 13·6 (13·95).
7. Metal 3·2 + 2O (at 1·6) 3·2 = 6·4 (6·59).
8. Mo 3·2 + 2O (at 2·4) 4·8 = 8·0 (8·33).
9. B 3·2 + 3O (at 1·6) 4·8 = 8·0 (8·26).
10. Metal 3·2 + 3O (at 2·4) 7·2 = 10·4 (9·51).
11. Metal 6·4 + 3O (at 2·4) 7·2 = 13·6 (14·26).
12. Sb 6·4 + 4O (at 2·4) 9·6 = 16·0 (15·3).
13. Ca 3·2 + F 6·4 = 9·6 (8·16); accords but little.
14. 2Metal 6·4 + Cl 6·4 = 12·8 (12·04).
15. Metal 6·4 + Cl 6·4 = 12·8 (12·40).
16. Metal 3·2 + Cl 6·4 = 9·6 (9·31).
17. Metal 3·2 + 2Cl 12·8 = 16·0 (18·69, but liquid).
18. P or As 6·4 + 3Cl 19·2 = 25·6 (30·36, but liquid).
19. Metal 6·4 + Br. 6·4 = 12·8 (12·71).
20. Pb 3·2 + Br. 6·4 = 9·6 (9·71).
21. 2Metal 6·4 + I 6·4 = 12·8 (13·0).
22. Metal 6·4 + I 6·4 = 12·8 (13·6).
23. Metal 3·2 + I 6·4 = 9·6 (9·63).
24. 2Cu 6·4 + S 3·2 = 9·6 (9·65).
25. Metal 3·2 + S 3·2 = 6·4 (5·7....6·3). This large variation makes it probable that sulphur enters into many of these compounds with a smaller capacity for heat, perhaps = 2·4.
26. Ag 6·4 + S 3·2 = 9·6 (9·26).
27. 2Bi 6·4 + 3S 9·6 = 16·0 (15·65).
28. If the carbon in this compound be supposed to possess 8 times the capacity for heat which it has in the diamond, or twice the normal capacity, we shall have: C 6·4 + 2S 6·4 = 12·8 (12·5).
29. Metal 3·2 + 2S 6·4 = 9·6 (10·36).
30. Fe 3·2 + 2S (at 2·4) 4·8 = 8·0 (7·7).
31. As 6·4 + 2S 6·4 = 12·8 (11·9).
32. As 6·4 + 3S (at 2·4) 7·2 = 13·6 (13·95).
33. Sb 6·4 + 3S (at 3·2) 9·6 = 16·0 (16·05).
34. Co 3·2 + As 6·4 = 9·6 (9·64).
35. Sn 3·2 + Bi 3·2 = 6·4 (6·6).

* These numbers refer to those in the first column [illegible]).

36. $2Sn$ 6·4 + Bi 3·2 = 9·6 (10·1).

37. $2Pb$ 6·4, Sb 6·4 = 12·8 (13·06).

38. Like 35; 39 like 36.

40. KO (K 6·4 + O 2·4) 8·8 + CO^2 (C 1·6 + $2O$ at 2·4 = 4·8) 5·6 = 14·4 (14·5....14·9).

41. Met. O (according to 3) 5·6 + CO^2 (according to 40) 5·6 = 11·2 (10·51): not sufficiently near.

42. Does not give a satisfactory result.

43. KO 8·8 + BO^3 (according to 9) 8·0 = 16·8 (16·8....16·9).

44. PbO (according to 3) 5·6 + BO^3 8·0 = 13·6 (13·27).

45. KO 8·8 + $2BO^3$ 16·0 = 24·8 (24·0....25·7).

46. PbO 5·6 + $2BO^3$ 16·0 = 21·6 (20·7).

47. KO 8·8 + CrO^3 (Cr 3·2 + $3O$, at 2·4 = 7·2) 10·4 = 19·2 (18·4).

48. KO 8·8 + $2CrO^3$ 20·8 = 29·6 (28·4).

49. HO (according to 2) 6·4 + SO^3 (S 3·2 + $3O$ at 1·6 = 4·8) 8·0 = 14·4 (17·1): does not agree.

50. KO 8·8 + SO^3 8·0 = 16·8 (16·4....16·6).

51. Met. O 5·6 + SO^3 8·0 = 13·6 (13·06).

52. $3PbO$ (3.5·6) 16·8 + PO^5 (P 6·4 + $5O$ at 1·6 = 8·0) 14·4 = 31·2 (32·46).

53. $2KO$ (2.8·8) 17·6 + PO^5 14·4 = 32·0 (30·5....31·7).

54. $2PbO$ (2.5·6) 11·2 + PO^5 14·4 = 25·6 (24·2)

55. CaO 5·6 + PO^5 14·4 = 20·0 (19·9).

56. $3PbO$ (3.5·6) 16·8 + AsO^5 14·4 = 31·2 (32·8).

57. KO 8·8 + AsO^5 14·4 = 23·2 (25·4).—Since KO, ClO^5 and KO, NO^5 exhibit the same capacity, that of ClO^5 and NO^5 as well as that of AsO^5 must be 14·4: hence nitrogen in nitric acid must have twice the usual capacity.

58. BaO 5·6 + NO^5 14·4 = 20·0 (17·8 ... 19·9).

59. CaO 5·6 + SO^3 8·0 + $2HO$ (2.6·4) 12·8 = 26·4 (23·6) : a very considerable difference.

H. Schröder (*Pogg.* 52, 269) proceeds upon the same principles. He likewise supposes that certain substances may possess different atomic heat-capacities according to the compounds in which they exist, and brings this alteration of the capacity of a substance into connection with the change in its equivalent volume: so that the heat-capacity of a body is smallest in that compound into which it enters with the smallest equivalent volume (*compare* pp. 73—78). Oxygen, *e. g.* enters with a capacity of 2·4 into those compounds in which its equivalent volume is 2·7 (atomic weight of oxygen = 8), viz. compounds of 1 atom of metal with 1 At. oxygen, of 2 At. metal with 3, and of 3 At. metal with 4 At. oxygen; and with the capacity of 1·8 ($\frac{3}{4}$ of 2·4) into those compounds in which its volume is 1·35, viz. compounds of 1 At. metal with 2 At. oxygen. Similarly, with the compounds of sulphur and other substances, as may be seen more in detail in the original memoir.

It may perhaps be regarded as certain that the heat-capacity of the atoms of compounds must be smaller, the more strongly their elements are condensed. This is likewise seen (not however in all cases) on applying the method of calculating condensation given on page 77. The smaller the divisor, the greater is the number of compound atoms in the same space, and the greater therefore is the condensation of the elements in the compound. According to page 77, the divisor for FeS^2, is 6; for MoS^2, 7; for SnS^2, 8;—and according to the table p. 249, the heat-capacity of FeS^2 is 7·702; of MoS^2, 9·864; and of SnS^2, 10·856.—These observa-

tions on the connection between the condensation and heat-capacity of elements in their compounds may suffice for the present, till the mode of calculating the condensation of elements in compounds shall have been determined with greater accuracy.

Avogadro's method of calculating the heat-capacity of compound atoms appears to be founded on hypotheses of too bold a character, and therefore inadmissible.

The capacity of bodies for heat may be attributed to their adhesion to that element; and this adhesion in the atoms of most bodies may be supposed to be of the same strength,—so that these atoms, when immersed in a uniform medium of heat and exposed to the same temperature, will absorb equal quantities of heat. Since the heat which is attached to bodies by adhesion and expands them has lost absolutely nothing of its elasticity, and leaves the bodies as soon the temperature of any neighbouring body becomes lower, even in the slightest degree, the heat thus retained in bodies is called *Free, Uncombined, Sensible Heat**.

Chemical Relations.

I. *Combinations of Heat with Ponderable Bodies, constituting Fluids.*

All ponderable fluids, whether liquids or gases, may be regarded as chemical combinations of ponderable substances with a certain excess of heat: in the absence of heat, all ponderable bodies would exist in the solid state.

Substances which are solid at comparatively low temperatures assume the liquid and gaseous states at higher temperatures. With this change in their state of aggregation, part of the heat becomes insensible, both to

* Clement & Desormes consider that even a vacuum has a certain capacity for heat, and they estimate this capacity at 0·41, that of an equal bulk of air being assumed = 1. But Gay-Lussac has shown that if a Torricellian vacuum be produced in a tube 0·075 metres in width, and containing a delicate thermometer, no heating or cooling takes place on alternately contracting and enlarging the empty space by moving the mercury quickly up and down, unless a portion of air be present (*Comp.* Prevost, *Ann. Chim. Phys.* 31, 429). On the other hand, Clement & Desormes admitted air into an imperfect vacuum produced by the air-pump, and attributed the rise of temperature thereby produced to that portion of heat which was driven out of the empty space by the air which entered. But this rise of temperature may be better explained on the supposition that the air still contained in the vessel, as well as that which first enters, is compressed by the portion which follows, and thus its specific heat is diminished. Aug. de la Rive & F. Marcet have also shown (*Bibl. univ.* 22, 265) that when a thermometer is placed in the vacuum, close to the opening at which the air enters, it sinks during the first two or three seconds when the air enters, and afterwards rises, showing that the air which first enters absorbs heat in consequence of its expansion, and afterwards evolves it when compressed by the portions which subsequently enter. The following experiment likewise gives a similar result. When oil-gas, compressed to 30 atmospheres, is made to flow into a cylinder 3 feet long, and closed at the further end, that end becomes very warm, and the end at which the gas enters very cold (*Qu. J. of Roy. Inst. N. S.* 2, 474; also *Schw.* 51, 106).—If capacity for heat be due to the adhesion of heat to ponderable bodies, such capacity can scarcely be ascribed to a vacuum. On the other hand, the presence of a certain quantity of heat in the vacuum cannot be denied. For the adhesion of the heat to the solid walls of the empty space cannot overcome its expansive force to such an extent as to prevent any of it from remaining in the empty space; and the hotter the walls are, the greater will be the quantity of heat left in the free unabsorbed state; or, according to the ordinary view, the opposite walls of the vacuum emit and receive rays of heat through it, and consequently, the vacuum must be filled with these rays of heat, crossing each other

the feelings and to the thermometer, being then in a state of chemical combination, and thereby deprived, to a certain extent, of its elasticity. When these bodies return to their former state of aggregation, this portion of heat is set free and again becomes sensible to the feelings and to the thermometer. The heat thus combined with ponderable bodies in the liquid state is thence called *Combined* or *Latent Heat*, inasmuch as its tendency to equilibrium is to a certain extent overcome by the adhesion of the ponderable substance; likewise *Heat of Fluidity*, inasmuch as it is regarded as the cause of fluidity in ponderable bodies. It is however probable that solid bodies also contain heat chemically combined with them, as will be seen by II.—It appears then that a body may contain heat in two states,—first, chemically combined,—secondly, retained by adhesion.

1. Formation of Liquids.

A solid body, situated in a cold medium into which heat is gradually introduced, becomes capable, when the medium has attained a certain temperature, of fixing a portion of the heat,—and, if subjected to external pressure, forms a liquid by combining with it. The temperature at which this fusion takes place—the *Melting Point* as it is called,—is very different in different substances. The greater their affinity for heat, the sooner do they fix it even when diffused through the medium in very small quantity; the smaller the affinity, the greater must be the quantity of heat collected in and about the bodies in order that its expansive tendency may be overcome by that affinity.—Alcohol is liquid at $-90°$, mercury fuses at $-40°$, ice above $0°$, sulphur at $+109°$, many metals below a red heat, others not till raised to the highest attainable temperatures, and carbon probably not at any temperature hitherto produced. Hence the distinction between *easily fusible* and *refractory substances*—*Corpora fusibilia* and *refractaria*. Those compounds only are infusible which decompose below their melting point; *e. g.* wood.—The liquefaction of many substances is preceded by a softening which renders their particles capable of sticking together: *e. g.* the welding of iron and other metals, baking of porcelain, softening of wax.

The melting point of each individual body is perfectly constant: for as long as any of the substance remains to be fused, it renders latent any quantity of heat which may be added in excess; and it is not till the fusion is quite complete, that a further accession of heat causes the temperature to rise. If, on the contrary, the quantity of heat in the surrounding medium be diminished, the liquid previously formed first gives up to the medium merely that uncombined portion of heat by which its temperature had been raised above the melting point; but if the temperature of the medium ultimately falls below the melting point, the tendency of the heat to diffuse itself through the surrounding medium overcomes its affinity for the solid body, the heat leaves the ponderable matter, and the latter returns to the liquid state. The temperature at which a body solidifies, or the *Freezing Point*, generally coincides with the melting point: for just as when heat is communicated to a solid body, the temperature of that body does not rise above its melting point, till it has absorbed the quantity of heat required to melt it,—so, on the other hand, a liquid does not generally cool below the melting point until completely solidified,—because, so long as any portion of the substance remains in the liquid state, the abstraction of heat from without is compensated by the conversion of latent into sensible heat. Nevertheless, some

liquids, *e. g.* water, when kept perfectly at rest, may be cooled several degrees below the melting point, and in many cases will solidify instantaneously, particularly when disturbed, the temperature at the same time rising to the melting point. (*Vid.* pp. 9, 10.)—Respecting the difficult freezing of water in vessels exhausted of air, *vid.* August and Kries. (*Pogg.* 52, 184, and 636.)

Pure water when agitated can be cooled but very little below the melting point; but with aqueous solutions of salts, even when they are strongly agitated, the cooling may be carried a degree or even several degrees below the melting point,—the material (whether glass, lead or copper, of which the vessel consists, appearing to have no influence on the result. (Despretz.)

a. Quantity of salt dissolved in 1000 parts of water.

b. Maximum of cooling, before solidification, of a saline solution contained in a copper vessel surrounded with a freezing mixture and stirred.

c. Melting point, or temperature at the commencement of solidification.

Dry Carbonate of Soda.			Dry Carbonate of Soda.		Common Salt.		Chloride of Sodium.	
a.	*b.*	*c.*	*b.*	*c.*	*b.*	*c.*	*b.*	*c.*
6·173	1·79°	0·19°	1·21°	0·24°	0·42°	0·36°	1·38°	0·23°
12·346	2·29	0·37	1·53	0·16	1·20	0·71		0·53
24·692	2·41	0·76	1·44	0·95	2·25	1·41	1·12	1·03
37·039	2·73	1·16			2·77	2·12	3·92	1·61
74·078	2·26	1·26			5·35	4·34	5·59	3·56
148·156	5·05	1·82			9·83	9·20	9·99	8·91

When more than 24·693 parts of carbonate of soda are dissolved in 1000 parts of water, the solution when agitated deposits crystals of the salt instead of ice. It is remarkable that the efflorescent, less soluble carbonate of soda lowers the freezing point of water more than carbonate of potash; on the other hand, the more soluble sulphate of soda lowers it further than sulphate of potash. (Despretz.)

When ice at 0° is mixed with an equal quantity of water at 75°, all the ice melts and the water produced has the temperature of 0°. Consequently, 75 degrees of heat (= 135° Fah.) are absorbed from the water and enter into a state of chemical combination, in order to convert an equal quantity of ice at 0° into water at 0°. If water at 0° be mixed with ice below 0°, the water freezes,—and the temperature of the ice, when the right proportions have been observed, rises to 0°. 1lb. of ice at − 75° mixed with 1lb. of water at 0° would give 2lb. of ice at 0°. In this case, latent heat is set free and raises the temperature of the ice.

Whilst, according to this result, the latent heat of water appears to be 75°, that of tin is only 13·314°, and of lead 5·358°. (Rudberg, *Pogg.* 19, 125; *comp.* G. A. Erman, A. & F. Swanberg, Despretz, *Pogg.* 20, 282; 26, 291; 52, 177). According to the last mentioned observers, latent heat, like specific heat, appears to vary nearly in the inverse ratio of the atomic weights of the bodies.

¶ De la Provostaye & Desains make the latent heat of water = 79·25 C.; Regnault found it to be 79·24 by one experiment, and 79·06 by another. The mean of these results is 79·2° = 142·6° (Fah.)

Person (*Pogg.* 70, 300; *N. Ann. Chim. Phys.* 21, 295; abstr. *Ann. Chem. Pharm.* 74, 179) has determined the latent heat of fusion of 13 substances, and likewise their specific heat in the liquid state. The following are the results:

Latent Heat.

Substances.	Melting point.	Latent Heat for the unit of weight.
Tin	235° C.	14·3°
Bismuth	270	12·4
Lead	332	5·15
Zinc	423	27·46
D'Arcet's alloy, $Pb^2 Sn^2 Bi^3$	96	5·96
Fusible metal, $Pb Sn^2 Bi$	145	7·63
Phosphorus	44·2	5·034
Sulphur	115	9·368
Nitrate of soda	310·5	62·98
Nitrate of potash	339	47·371
Phosphate of soda, $P O^5$, 2Na O, 24H O	36·4	54·65
Chloride of calcium, Ca Cl, 6H O	28·5	45·79
Bees-wax (yellow)	62·0	43·51

Specific Heat.

Substances.	Temperatures between which the specific heat was determined.	Specific Heat.
Tin	340° and 240° C.	0·061
Bismuth	370 ,, 280	0·035
Lead	440 ,, 340	0·039
D'Arcet's alloy, $Pb^2 Sn^2 Bi^3$	300 ,, 136	0·036
,, ,,	136 ,, 107	0·047
,, ,,	80 ,, 14	0·060
,, ,,	50 ,, 12	0·049
Fusible metal, $Pb Sn^2 Bi$	330 ,, 143	0·046
Phosphorus	100 ,, 50	0·2045
Sulphur	147 ,, 120	0·234
Nitrate of soda	430 ,, 330	0·413
Nitrate of potash	435 ,, 350	0·33186
Phosphate of soda, 2Na O, $P O^5$ + 24H O	79 ,, 44	0·758
,, ,,	2 ,, −20	0·454
Chloride of calcium, Ca Cl, 6H O	127 ,, 100	0·519
,, ,,	100 ,, 60	0·628
,, ,,	60 ,, 31	0·358
,, ,,	28 ,, 4	0·647
,, ,,	2 ,, −20	0·406
Beeswax (yellow)	102 ,, 66	0·54
,, ,,	58 ,, 42	0·72
,, ,,	42 ,, 26	0·79
,, ,,	26 ,, 6	0·52
,, ,,	2 ,, −20	0·39
Ice	0 ,, −30	0·504

The latent heat l of these bodies may be expressed by the formula

$$(160 + t)\,\delta = l$$

where t denotes the melting point in centigrade degrees, $\delta = C - c$ the

difference of specific heat in the solid ($= c$) and the liquid state ($= C$). For example, we have

Substances.	Melting point.	Specific Heat in the		Latent Heat.	
		solid state.	liquid state.	observed.	calculated.
Water	0°	0·504	1·0000	79·25	79·20
Phosphorus	44·2	0·1788	0·2045	5·034	5·243
Sulphur	115	0·20295	0·234	9·368	9·350
Nitrate of soda ...	310·5	0·27821	0·413	62·975	63·4
,, potash..	339	0·23875	0·33186	47·371	46·462

The above equation shows that—*To obtain the latent heat of a body, the difference of its two specific heats must be repeated as many times as there are degrees between* $-160°$ *and its melting point.*

From this it is probable that $-160°$ C. or $-256°$ F. is the absolute zero of heat; since otherwise we shall be obliged to admit that, at temperatures below $-160°$, the difference between the specific heats in the solid and liquid states must for all bodies be equal to nothing.

The preceding formula is not applicable to the metals, inasmuch as for these bodies the value of δ is almost nothing. Person is however of opinion that if the metals could be retained in the liquid state below their ordinary melting points, their specific heat ($= C$) in this state would be found to be much greater than it is at temperatures above the melting point, and consequently $\delta = C - c$ would have a more considerable value.

According to Person, the latent heat of fluidity is not a constant quantity, but, like the latent heat of vaporization, *variable with the temperature.* Thus, 1 kilogramme of ice at $-20°$ C. requires 10 units of heat to bring it to 0° and 79·2 units to melt it; in all therefore 89·2 units. Now if water at 0° be cooled to $-20°$, it loses 20 units of heat,—since, according to Person's experiments, the specific heat of water does not alter sensibly at temperatures below 0°. Consequently, when it freezes, it can only give up $89·2 - 20 = 69·2$ units of heat. ¶.

Most bodies contract in passing from the liquid to the solid state; the following only are known to expand in undergoing this change: water, bismuth, and cast-iron, according to Reaumur; copper, according to Karsten; silver according to Persoz (*Chim. molecul.* 240); certain alloys of bismuth, and likewise oxide of lead, according to Manx. The expansion of antimony, observed by Reaumur, is not confirmed by the experiments of Manx. Water, according to Leroyer & Dumas, expands in freezing by $\frac{1}{9}\frac{1}{0}$ of its volume; bismuth, according to Manx, at least $\frac{1}{1}\frac{1}{3}$. Solid pieces of these substances float on the melted portion. The outer portion of these liquids being generally the first to solidify, the enclosed portion which still remains liquid splits the solid crust or the vessel in cooling, and forms an opening by which a portion flows out. Melted bismuth drawn up into a glass tube bursts it in solidifying. (Marx, *Schw.* 58, 454; *J. pr. Chem.* 22, 135.) This expansion seems to be connected with the fact that such bodies, water, *e. g.*, attain their greatest density several degrees above their freezing points, and when cooled below the particular temperature which gives the maximum density, expand more and more as they approach the freezing point. (p. 225.)

Metallic alloys often exhibit two solidifying points, that is to say,—

when the melted mass is cooling, the temperature remains constant for some time at two different points. This takes place when the metals are not combined in the stoichiometrical proportion in which they unite into a solid compound: in such a case the metal which is in excess solidifies first, and the more intimate compound at a lower temperature. (*Pogg.* 18, 240.)

On the compressibility of liquids—which is of very small amount, and at least in the case of water follows Mariotte's law—*vid.* Oersted (*Schw.* 52, 9); Colladon & Sturm. (*Ann. Chim. Phys.* 35, 113; also *Pogg.* 12, 39, and 161.)

2. Vaporization.

All ponderable substances have an affinity for heat, in consequence of which they endeavour to combine with it and form *Elastic Fluids* or *Gases*. Every gas consists, therefore, of heat and a ponderable substance, the *Ponderable Basis* or *Material*.

This affinity differs greatly in amount. Substances which have great tendency to assume the gaseous form are called *Volatile;* those in which this tendency is small are called *Fixed; Corpora volatilia* and *fixa*. On the whole, the volatility of bodies follows the same order as their fusibility; nevertheless, water is more volatile than mercury or oil of vitriol. —The more intimate the union between the ponderable body and heat, the greater is the difficulty of depriving the body of its gaseous form by external pressure and cooling,—the more permanent, therefore, is the gas. A gradual transition nevertheless exists from those gases which are either not condensable at all, like oxygen, or only by very strong pressure and cooling, like carbonic acid,—to those which, like the vapour of iron, exist only at the highest known temperatures. Gases may therefore be divided into *Permanent Gases*, which retain their gaseous form under the ordinary atmospheric pressure and at 0°, and *Vapours* which, under these circumstances, return to the liquid or the solid state.

Heat is contained in gases in larger quantity than in liquids; it predominates in them, overcomes the cohesion of their ponderable matter, and imparts to them, on the contrary, a tendency to expand without limit when not prevented by external obstacles. This expansive tendency of gases is their *Elasticity* or *Tension*. In the same gas, and at the same temperature, the tension varies, according to Mariotte's law, in the direct ratio of the density.—It is only when gases are brought by pressure and cooling near the point at which they assume the liquid form, that the density increases somewhat more rapidly than the elasticity.—This peculiarity is exhibited not only by vapours, but also by those more permanent gases which may be liquefied by strong pressure, *e. g.*, sulphuretted hydrogen, ammonia, cyanogen, and (according to Oersted) sulphurous acid gas. If equal measures of air and ammoniacal gas are exposed to the same pressure, the latter is condensed in a higher degree, as if it were exposed to a stronger pressure, and this difference increases considerably as the pressure becomes greater:

Air	1·819 Met....	2·582 Met....	3·863 Met.
Ammoniacal gas....	1·850 ,,	2·663	4·132 ,,

A condensation of air corresponding to a pressure of 3·863 met. of the mercurial column, produces, therefore, the same condensation of ammoniacal gas as if the pressure were that of a column of 4·132 met. (Despretz, *Ann. Chim. Phys.* 34, 335, and 443; also *Pogg.* 9, 605; also *Schw.* 51,

108.)—Even carbonic acid gas, which is not so easily liquefied as the gases just mentioned, has a density somewhat too great, even under the ordinary pressure; it does not exactly follow Mariotte's law, till the pressure is reduced to less than ½ of an atmosphere. (Wrede, *Ann. Pharm.* 38, 140.)*

All ponderable substances, when in the gaseous form, are reduced to their utmost state of expansion and rarity, and pass through openings which are impervious to liquids and solids. All gases are transparent; most of them colourless.—The gases of chlorine, oxide of chlorine, selenium, and sulphur, are yellow,—of bromine and hyponitric acid red,—of iodine violet,—and of indigo reddish purple.

A. *Conditions of Vaporization.*

a. A certain space must be allowed.

Every ponderable substance takes up a greater space in the gaseous than in the liquid or solid state. If, therefore, a solid or liquid body be closely confined by an unyielding envelope, no formation of gas can take place at any temperature, unless the envelope be burst open. If, on the contrary, the body be situated in a vacuum, a portion of it—corresponding to the magnitude of the empty space, the temperature, and the nature of the substance itself—will be converted into gas.

When a certain quantity of gas has been generated in an empty space, the expansive tendency of the gas already produced hinders the further vaporization of the remaining substance: for this would produce compression of the gas previously formed. Equilibrium is therefore established between the elasticity of the generated gas and the tendency of the remaining matter to combine with heat and form more gas,—and thus the further production of gas is prevented. The empty space is now *saturated*, as it were, with gas at the given temperature, or a *saturated gas* has been produced. But if the *temperature* be raised, the affinity of the heat for the remaining matter will overcome the elasticity of the gas previously generated, and a further production of gas will take place: a larger quantity of gas is thus accumulated in the same space,—in consequence of which the elasticity increases, and gradually attains such a degree of force that equilibrium is again established, and the further accumulation of gas is stopped. The higher therefore the temperature, the greater is the quantity of matter vaporized in vacuo, and the greater are the density and elasticity of the gas or vapour produced.

The gas contained in any space is *unsaturated*, when an additional quantity of the same vaporizable substance introduced into it is likewise converted into gas. Thus carbonic acid gas, at ordinary pressures and temperatures, is an unsaturated gas; for liquid carbonic acid introduced into a space filled with it vaporizes in large quantity,—and it is not till the vaporization is ended, and a portion of carbonic acid still remains liquid, that the gas can be regarded as saturated. The same is true of all gases which are permanent at ordinary pressures and temperatures.

Alcohol, ether, or rock-oil enclosed in a tube of strong glass or iron is completely converted into vapour on the application of heat, only when the space not occupied by the liquid is somewhat greater than the volume of the liquid itself. With rock-oil the empty space may be somewhat smaller than with alcohol, and with ether still less. Alcohol when *thus*

* See also Regnault. (*Pogg.* 77, 531.)

heated acquires increased mobility; expands to twice its original volume, and is then suddenly converted into vapour;—this change takes place at 207° C. (404·6° Fah.), when the alcohol occupies just half the volume of the tube. If the tube is more than half filled with alcohol, it bursts when heated. A glass tube one-third filled with water becomes opaque when heated, and bursts after a few seconds. If this chemical action of the water on the glass be diminished by the addition of a little carbonate of soda, the transparency of the glass will be much less impaired; and if the space occupied by the water be $\frac{1}{4}$ of the whole tube, the liquid will be converted into vapour at about the temperature of melting zinc. (Cagniard de la Tour.)—If liquid carbonic acid sealed in a glass tube occupies $\frac{3}{10}$ of the volume of the tube at 0°, it neither increases nor diminishes in bulk when heated, because the increase of volume produced by heating is just compensated by the diminution caused by vaporization. If it occupies $\frac{1}{3}$ of the space at 0°, its volume diminishes when it is heated, and increases when it is cooled, because the loss by evaporation preponderates over the expansion. If it takes up $\frac{2}{3}$ of the space, its volume increases by heat and contracts by cold, as in a thermometer; but at + 30° (86° Fah.) the whole is converted into vapour. The gas, which at 0° occupies the space above the liquid carbonic acid would, if condensed, yield $\frac{1}{1\cdot3}$ of its volume of liquid acid; and that which is produced at + 30° would give $\frac{1}{5}$ ($\frac{2}{3}$? Gm.) of its volume of liquid carbonic acid at 0°. (Thilorier.)

When a volatile substance is heated, the tension of the gas increases in a much higher ratio than its density, because the heat not only increases the elasticity by producing more gas, but likewise by its expanding force imparts a higher degree of elasticity to the gas already formed. In the case of water the following table has been calculated by Despretz.

Temperature.	Elasticity.	Actual Density.	Density corresponding to the Elasticity.	Difference.
0° C.	0·005 Met.	1·00	1·0	0
25	0·023	4·20	4·6	0·2
50	0·089	14·90	17·8	2·9
75	0·285	44·49	57·0	12·5
100	0·769	110·54	152·0	41·46
120	1·449	199·86	289·8	89·94
140	2·356	308·98	471·2	162·22
163	3·571	443·32	714·2	270·88

The higher the temperature the greater is the difference; hence the advantage of high-pressure steam-engines. (Despretz.)

Lastly, when the volume of the empty space and the temperature are given, the quantity of gas produced varies with the *nature of the body:* 1. According to the affinity between the ponderable matter and heat: for the weaker this affinity, the smaller will be the quantity of gas which by its tension will be able to stop the further production of gas; and the greater the affinity, the denser and more elastic must be the gas produced before the process of evaporation ceases;—2. According to the atomic weight of the substance: for the atomic weight is closely connected with the specific gravity of the gas (pp. 52 and 64).

The most volatile among terrestrial substances, so far as they have not been prevented by combination with others, have especially assumed the gaseous form; and the aeriform mixture thus produced constitutes the *Atmosphere* or *Common Air* surrounding the earth. The weight with which this mass of air presses on the earth's surface varies with atmo-

spheric changes and with the height of the locality. At the level of the sea it is nearly equal to the pressure which would be produced by a column of mercury of the height of 28 Paris inches 0·9 line, or 29·92 English inches, or 0·76 metre; and the pressure corresponding to this height is taken as the normal barometric pressure, and called *Atmospheric Pressure, Pressure of the Atmospheric Column, Atmosphere.* If a glass tube about 1 metre in length, and closed at one end, be carefully filled with mercury and inverted in that liquid, the pressure of the air acts in such a manner that the mercury within the tube stands about 0·76 met. above the level of that without. The space above the mercurial column is called the *Torricellian vacuum.* The pressure of the atmosphere amounts to about 15 lbs. on a square inch of surface, or 1033 grammes on a square centimetre.

A volatile body at the surface of the earth is placed, as it were, in a vessel with moveable sides, which press it in all directions with a force equivalent to the weight of a column of mercury 0·76 met. high. If the body is enclosed in a flexible bag, or shut off by mercury or in any other manner from the immediate contact of the air, its conversion into vapour will not take place unless the elasticity of its vapour at the given temperature be at least equal to the atmospheric pressure, or sufficient to support a column of mercury 0·76 met. high. Since, however, this elasticity increases with the temperature, there exists for each body a certain temperature at which the elasticity of its vapour is a balance for the pressure of the atmosphere, and consequently cannot be restrained by that pressure. This temperature is the *Boiling Point* of the body. At this point it passes into vapour, in spite of the atmospheric pressure, as soon as the additional heat required to volatilize it is supplied.

If a substance, the tension of whose vapour at the given temperature is less than the atmospheric pressure, be introduced in excess into the Torricellian vacuum—that is to say—into a space in which the pressure of the atmosphere is balanced by a corresponding column of mercury, the substance fills the empty space with vapour having an elasticity corresponding to the temperature. By this the column of mercury in the barometer-tube is depressed through a height corresponding to the elasticity: for the tension of the vapour now supplies the place of part of the column of mercury. In this manner the elasticity of a vapour, when less than the atmospheric pressure, may be estimated in lines or millimetres of the mercurial column.

If heat be now applied to the unvaporized portion of the body situated in the vacuum, the density and elasticity of the vapour increase; the vapour depresses the mercury more and more, the higher the temperature is raised, and the more elastic the vapour in consequence becomes; till at length the mercury within the barometer-tube stands at the same level as that without. This temperature again is the boiling point: for the tension of the vapour is now of itself a balance for the pressure of the air.

As the atmospheric pressure increases or diminishes, the boiling point —or temperature at which the body assumes the gaseous form—rises or falls; it is usual, however, to state the boiling-point as corresponding to a pressure of 0·76 metre.

In the following data of the elasticities of different gases, it is to be observed that the gas or vapour is supposed to be in contact with unvaporized matter; and therefore that a saturated vapour or gas is produced. The more permanent gases are exposed to the different temperatures in contact with unvaporized matter in a sealed tube, a narrow gradu-

ated glass tube filled with air and closed with a drop of mercury (*Manometer*) being placed in the same tube to indicate the pressure by the various degrees of compression of the enclosed air. The more volatile substances are introduced into the Torricellian vacuum, where they depress the mercurial column in proportion to the elasticity of their vapours.

The elasticity of the more permanent gases is expressed in whole atmospheres. In this table, D F denotes Davy & Faraday (*Phil. Trans.* 1823, 160 and 189); N, Niemann (*Br. Archiv.* 36, 175); B, Bunsen (*Pogg.* 46, 95); T, Thilorier (*Ann. Chim. Phys.* 60, 434); M, Mitchell (*Sill. Amer. J.* 1840, 177, also *Ann. Pharm.* 37, 354).

		Degrees below 0.									Degrees above 0.									
		33·7	20	16	15	11	10	5	4	0	5	6·4	7·2	10	10·6	12·5	15	20	25	30
Nitrous oxide	DF	.	.	.	.	.	.	.	.	44	.	.	51	*	.	.	.	.	.	.
Carbonic acid	DF	.	.	.	.	20	.	.	.	36	.	.	.	.	.	.	.	.	.	.
	T	.	26	.	.	.	.	.	.	36	.	.	.	.	.	.	.	.	.	73
	M	.	.	.	.	.	.	.	.	36	.	45	.	.	60	.	.	.	.	72
	N	.	.	.	.	.	.	.	.	40	.	.	.	.	.	60	.	.	.	.
Oxide of chlorine	DF	.	.	.	.	.	.	.	.	.	.	.	40	.	.	.	.	.	.	.
	N	.	.	.	.	.	.	.	.	.	.	.	.	.	.	60	.	.	.	.
Hydrochloric acid	DF	.	.	20	.	.	.	.	25	.	.	.	.	.	40	.	.	.	.	.
	N	.	.	.	.	.	.	.	.	33	.	.	.	.	.	40	.	.	.	.
Sulphuretted hydrogen	DF	.	.	14	.	.	.	.	.	.	.	.	.	17	.	.	.	.	.	.
	N	.	.	.	.	.	.	.	.	54	.	.	.	.	.	58	.	.	.	.
Ammonia	DF	.	.	.	.	.	.	.	.	5	.	.	.	6·5	.	.	.	.	.	.
	N	.	.	.	.	.	.	.	.	.	.	.	.	.	.	7	.	.	.	.
	B	1	.	.	.	.	.	4	.	4·8	5·6	.	.	6·5	.	.	7·6	8·8	.	.
Cyanogen	DF	.	.	.	.	.	.	.	.	.	.	.	3·6	.	.	.	.	.	.	.
	N	.	.	.	.	.	.	.	.	.	.	.	.	.	.	4	.	.	.	.
	B	.	1·05	.	1·45	.	1·85	2·3	.	2·7	3·2	.	.	3·8	.	.	4·4	5	.	.
Chlorine	DF	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	4	.	.	.
	N	.	.	.	.	.	.	.	.	6·5	.	.	.	.	.	8·5	.	.	.	.
Sulphurous acid	DF	.	.	.	.	1	.	.	.	.	.	.	2	.	.	.	.	.	.	.
	N	.	.	.	.	.	.	.	.	.	.	.	.	.	.	3	.	.	.	.
	B	.	.	.	.	.	1·03	1·5	.	1·94	.	.	.	3·15	.	.	3·85	4·6	5·5	.

According to Oerstedt and Swendson, the tension of sulphurous acid at + 21·25° amounts to 3·269 atmospheres.

According to Wach (*Schw.* 50, 33), the tension of sulphurous acid at 6·75 = 3·2 and at 19·5° = 4·36 atmospheres.—The boiling-point of sulphurous acid (at a pressure of 0·76 metre) is about − 10°, that of cyanogen − 20°, of ammonia − 33·7°, and of carbonic acid about − 50°. Phosphuretted hydrogen, hydriodic acid, hydrobromic acid, and hydrochloric acid gases may, according to Bunsen, be liquefied by cooling to − 90°.

The elasticity of vapours is expressed sometimes in atmospheres, sometimes in metres, sometimes in inches and lines. The tension of the vapour of water at low temperatures is the mean tension calculated by Kämtz (*Schw.* 42, 385) from the experiments of Rouppe, Schmidt, and Ure; that of the same vapour at high temperatures is given by Arago and Dulong (*Ann. Chim. Phys.* 43, 74; also *Pogg.* 18, 437; also *Schw.* 59, 167); that of vapour of mercury by Avogadro (*Ann. Chim. Phys.* 49, 369); that of the vapour of sulphuret of carbon by Marx (*Schw.* 62, 460), and those of the vapours of alcohol, ether, rock-oil, and oil of turpentine by Ure. (*Phil. Trans.* 1818, p. 338; also *Schw.* 28, 328.) Some of the following series are merely extracts. Degrees of Reaumur and Fahrenheit will also be found here and there.

* According to a former statement, 5.

Vapour of Water.				Vapour of Mercury.		Vapour of Sulphuret of Carbon	
Kämtz.		Arago & Dulong.		Avogadro.		Marx.	
	Par. Lin.		Atm.		Metres.		
0° R.	2·10	100° C.	1	100° C.	0·00003	− 8·75° C.	32·00
+ 5	3·09	112·2	1·5	110	0·00007	− 5	40·36
10	4·62	121·4	2	120	0·00016	0	58·50
15	6·98	128·8	2·5	130	0·00035	+ 5	71·00
20	10·08	135·1	3	140	0·00073	10	87·30
25	14·32	140·6	3·5	150	0·00143	15	106·75
30	20·35	145·4	4	160	0·00261	20	129·37
35	28·59	149·06	4·5	170	0·00458	25	156·21
40	39·23	153·08	5	180	0·00771	30	187·62
45	54·07	156·8	5·5	190	0·01245	35	224·32
50	72·80	160·2	6	200	0·01930	40	264·37
55	96·59	163·48	6·5	210	0·02880	45	312·12
60	126·34	166·5	7	220	0·04154	50	367·62
65	163·88	169·37	7·5	230	0·05801	55	431·50
70	211·20	172·1	8	240	0·07865	59·37	494·00
75	268·33	177·1	9	250	0·10378		
80	336·00	181·6	10	260	0·13362		
85	425·33	186·03	11	270	0·16830		
90	525·29	190	12	280	0·20790		
95	644·56	193·7	13	290	0·25251		
100	789·05	197·19	14	300	0·30233		
105	948·79	200·48	15	310	0·35775		
110	1155·9	203·6	16	320	0·41938		
115	1358·8	206·57	17	330	0·48838		
120	1612·1	209·4	18	340	0·56637		
		212·1	19	350	0·65577		
		214·7	20	360	0·76000		
		217·2	21				
		219·6	22				
		221·9	23				
		224·2	24				
		226·3	25				
		236·2	30				
		244·85	35				
		252·55	40				
		259·52	45				
		265·89	50				

Alcohol.		Ether.		Rock-oil.		Oil of Turpentine.	
Ure.		Ure.		Ure.		Ure.	
	Engl. in.		Engl. in.		Engl. in.		Engl. in.
32° F.	0·40	+ 34 F°	6·2	+ 316° F.	30·0	+ 304° F.	30
40	0·56	44	8·14	320	31·7	310	33·5
50	0·86	54	10·3	325	34·0	315	35·2
60	1·23	64	13·0	330	36·4	320	37·1
70	1·76	74	16·1	335	38·9	322	37·8
80	2·45	84	20·0	340	41·6	326	40·2
90	3·40	94	24·7	345	44·1	330	42·1
100	4·50	104	30·0	350	46·9	336	45·0
110	6·00	110	32·5	355	50·2	340	47·3
120	8·10	120	39·5	360	53·3	343	49·4
130	10·60	130	47·1	365	[illegible]	347	51·7
140	13·9	140	56·0			350	53·8
150	18·0	150	[illegible]			54	56·6

Alcohol.		Ether.		Rock-oil.		Oil of Turpentine.	
Ure.	Engl. in.	Ure.	Engl. in.	Ure.	Engl. in.	Ure.	Engl. in.
160	22·6	160	80·3	375	64·0	357	58·7
170	28·3	170	92·8			360	60·8
173	30·0	180	108·3			362	62·4
180	39·7	190	124·8				
190	43·2	200	142·8				
200	53·0	210	166·0				
206	60·1						
210	65·0						
220	78·5						
230	94·1						
240	111·2						
250	132·3						
260	155·2						

The tension of the vapour of sulphuret of carbon at 12° C. amounts to 0·2 metre (Berzelius & Marcet); at 22·5° to 0·3184 M. (Cluzel); at 46·6° to 0·76 M. (Gay-Lussac); at 57·6° to 1½, at 160° to 7·7, and at 171° to 8·95 atmospheres. (Davy & Faraday.)—On the tension of the vapours of water, alcohol, and ether, *comp.* Dalton (*Ann. Phil.* 15, 130) and August. (*Pogg.* 13, 122.)

[Calculation of the tension of aqueous vapour at different temperatures by F. Von Wrede. (*Pogg.* 53, 225.)]

¶ Magnus (*Pogg.* 61, 225) and Regnault (*N. Ann. Chim. Phys.* 11, 334; 13, 196) have also determined the tension of the vapour of water at different temperatures. The results obtained by these philosophers, whose experiments were made independently of each other, present the most remarkable agreement, as will be seen from the following table.

Temp. C.	Tension in Millimetres.		Temp. C.	Tension in Millimetres.	
	Magnus.	Regnault.		Magnus.	Regnault.
−32°		0·310	9	2·284	2·137
31		0·336	8	2·471	2·327
30		0·365	7	2·671	2·533
29		0·397	6	2·886	2·758
28		0·431	5	3·115	3·004
27		0·468	4	3·361	3·271
26		0·509	3	3·624	3·553
25		0·553	2	3·905	3·879
24		0·602	1	4·205	4·224
23		0·654	0	4·525	4·600
22		0·711	+ 1	4·867	4·940
21		0·774	2	5·231	5·302
20	0·916	0·841	3	5·619	5·687
19	0·999	0·916	4	6·032	6·097
18	1·089	0·996	5	6·471	6·534
17	1·186	1·084	6	6·939	6·998
16	1·290	1·179	7	7·436	7·492
15	1·403	1·284	8	7·964	8·017
14	1·525	1·398	9	8·525	8·574
13	1·655	1·521	10	9·126	9·165
12	1·796	1·656	11	9·751	9·792
11	1·947	1·803	12	10·421	10·457
10	2·109	1·963	13	11·130	11·162

Temp. C.	Tension in Millimetres.		Temp. C.	Tension in Millimetres.	
	Magnus.	Regnault.		Magnus.	Regnault.
14	11·882	11·908	67	203·975	204·376
15	12·677	12·699	68	213·166	213·596
16	13·519	13·536	69	222·706	223·165
17	14·409	14·421	70	232·606	233·093
18	15·351	15·357	71	242·877	243·393
19	16·345	16·346	72	253·530	254·073
20	17·396	17·391	73	264·577	265·147
21	18·505	18·495	74	276·029	276·624
22	19·675	19·659	75	287·898	288·517
23	20·909	20·888	76	300·193	300·838
24	22·211	22·184	77	312·934	313·600
25	23·582	23·550	78	326·127	326·811
26	25·026	24·988	79	339·786	340·488
27	26·547	26·505	80	353·926	354·643
28	28·148	28·101	81	368·558	369·287
29	29·832	29·782	82	383·697	384·435
30	31·602	31·548	83	399·357	400·101
31	33·464	33·406	84	415·552	416·298
32	35·419	35·359	85	432·295	433·041
33	37·473	37·411	86	449·603	450·344
34	39·630	39·565	87	467·489	468·221
35	41·893	41·827	88	485·970	486·687
36	44·268	44·201	89	505·060	505·759
37	46·758	46·691	90	524·775	525·450
38	49·368	49·302	91	545·133	545·778
39	52·103	52·039	92	566·147	566·757
40	54·969	54·906	93	587·936	588·406
41	57·969	57·910	94	610·217	610·740
42	61·109	61·055	95	633·305	633·778
43	64·396	64·346	96	657·120	657·535
44	67·833	67·790	97	681·683	682·029
45	71·427	71·391	98	707·000	707·280
46	75·185	75·158	99	733·100	733·305
47	79·111	79·093	100	760·000	760·000
48	83·212	83·204	101	787·718	
49	87·494	87·499	102	816·273	
50	91·965	91·965	103	845·683	
51	96·630	96·661	104	875·971	
52	101·497	101·543	105	907·157	
53	106·572	106·636	106	939·260	
54	111·864	111·945	107	972·296	
55	117·378	117·478	108	1006·300	
56	123·124	123·244	109	1041·278	
57	129·109	129·251	110	1077·261	
58	135·241	135·505	111	1114·268	
59	141·829	142·015	112	1152·321	
60	148·579	148·791	113	1191·444	
61	155·603	155·839	114	1231·660	
62	162·908	163·170	115	1272·986	
63	170·502	170·791	116	1315·462	
64	178·397	178·714	117	1359·094	
65	186·601	186·945	118	1403·915	
66	195·124	195·496			

These measurements, as far at least as temperatures within fifteen
sixteen degrees of 100° C. are concerned, have also been confirmed in
remarkable manner by determinations of the boiling-point of water at di
ferent heights on the Pyrenees, and also on Mont Blanc (*Vid. Pogg.* 7
pp. 360, 365, 368; also *Ann. Chim. Ph.*

The progression of the tension is not affected by the freezing-point, at least in the case of water and hydrocyanic acid; at 0° ice and water have the same tension; it is not, therefore, affected by the greater cohesion of ice. (Gay-Lussac, *Ann. Chim. Phys.* 70, 419.)

Volta's (*Schw.* 52, 98) and Dalton's law, according to which the vapours of different substances have the same tension at an equal number of thermometric degrees above or below their boiling-points, is regarded as incorrect by Schmidt, Mayer, Despretz, Ure, and others, according to the results of their own experiments: it is nevertheless remarkable that this law is pretty nearly true in the case of many substances. From the boiling-point of sulphurous acid, *e. g.* to the temperature at which its tension is equal to 2 atmospheres, there is, according to the preceding table, an interval of 17° C.; in the case of water, the corresponding interval is about 20°; of alcohol 18°, and of ether 20°: but in the case of rock-oil and oil of turpentine, which are liquids of less simple constitution, it is about 30°. Davy also (*Ann. Chim. Phys.* 20, 175) puts forward a view founded on his experiments with sulphuret of carbon, chloride of phosphorus, and alcohol, favourable to Dalton's law.—Dove's (*Pogg.* 23, 291) comparison of the tensions of permanent gases, according to Faraday, with that of vapour of water according to Arago and Dulong, likewise speaks in favour of this law.

	Atmosph.	Nitrous oxide.	Water.	Atmosph.	Carb. Acid.	Water.
	50	+ 7·2	+ 265·9	36	0°	+ 246·4
	44	0	+ 258·2	20	− 11·1	+ 234·7
Diff.....	6	7·2	7·7°	16	11·1	11·7

	Atmosph.	Hydrochl. Acid.	Water.	Atmosph.	Ammonia.	Water.
	25	− 3·9°	+ 226·3°	6·5	+ 10°	+ 163·48°
	20	− 16·1	+ 214·7	5	0	+ 153·08
Diff.....	5	12·2	11·6	1·5	10	10·4

Sulphurous acid is also nearly in accordance with the law, but sulphuretted hydrogen is not; respecting this last gas, however, it must be observed that the determinations of its tension by Davy & Faraday and by Niemann differ considerably. According to this law, the boiling-point of nitrous oxide should be − 158°, of carbonic acid − 146°, of hydrochloric acid − 130°, and of ammonia − 53° (Dove); according to Bunsen, however, the boiling point of ammonia is 33·7°.

If a substance B be enclosed in a space already filled with the vapour of another substance A, which may be atmospheric air or any other gas,—no portion of A being present in the non-gaseous form, B being in immediate contact with A, and the two substances not being capable, under the given circumstances, of entering into chemical combination with one another,—then, whether the elasticity of the gas produced by B be greater or less than that of the gas A, B will produce exactly the same quantity of gas as if it were situated in a vacuum at the same temperature,—with this difference, however, that in the first case the conversion of B into gas takes place almost as quickly as if it were in vacuo; in the second very slowly and only on the surface, where the gas A is in contact with the

substance B. The effect takes place more or less quickly in proportion to the rarity or density of the gas A. (Volta, *Schw.* 52, 98, Dalton.)

Ice evaporates in the open air at temperatures much below 0°: the chlorides of potassium, sodium and antimony do not evaporate at a red heat in a covered crucible; but when the crucible is opened, and a current of air thereby produced, vaporization takes place. Zinc volatilizes in carbonic oxide gas (when oxide of zinc is ignited in contact with charcoal) at a lower temperature than when heated alone. Iodine, whose boiling point is 175°, passes over with vapour of water at 100°. (Gay-Lussac.) Similarly, water mixed with alcohol evaporates when heated, together with the alcohol vapour. When the aqueous solutions of different salts are evaporated, part of the salt is likewise given off; this may however be explained by supposing the salt to be mechanically carried over: at all events Faraday (*J. of Roy. Inst.* 1, 70; also *Pogg.* 18, 545) found that the water evaporated at ordinary temperatures from saline solutions is free from salt. The cases of reciprocal affinity from the mutual adhesion of gases likewise belong to this head. (pp. 125, 126.) —The more diffusible the gas, the more quickly do bodies evaporate in it; the effect takes place more quickly therefore in hydrogen gas.

It may be supposed that when the elasticity of the gas A is greater than that of the gas which would be produced from B at the given temperature, no part of B can be converted into gas, because the gas already present must by its elasticity compress the substance B sufficiently to prevent the vaporization. The formation of gas is likewise prevented when the substance B is separated from the gas A by a moveable sheet of matter, a bladder for example. The gas A must always be in immediate contact with the substance B, and the formation of gas takes place only at the points of contact. This phenomenon is explained by Berthollet (*Statique Chim.* 1, 280) on the hypothesis of a *chemical solution* of the gas B in the gas A,—with respect to which it must be particularly observed that neither the density nor the chemical nature, but only the volume of the gas A has any influence on the quantity of the gas B produced. Dalton, on the other hand, explains it by supposing—either that one gas acts as a vacuum to the other, or that the unequal magnitudes of the globules of the two gases give rise to an internal motion and uniform distribution of their particles. The phenomenon is perhaps best explained by supposing that the *adhesion* of the existing gas A for the gas B, which is to be produced, is in all cases more powerful than the pressure which A, whatever may be its density, exerts upon the substance B, inasmuch as the adhesion increases with the density,—and consequently, that the body B diffuses itself with its proper elasticity through any other gas in the same quantity as in vacuo. (*Compare* pp. 22, 23.)

When a gas B is generated within an unyielding envelope the interior of which is already occupied by another gas A, both gases together press against the sides, each with its own proper tension. If for example the tension of the gas A $= x$ and that of the gas B $= y$, the tension or elasticity of the gaseous mixture $= x + y$.

If, on the contrary, the sides of the vessel in which the gaseous mixture is generated yield to such an extent that the gas remains constantly under the pressure x, the mixed gases first expand (since according to Mariotte's law the elasticity of a gas varies inversely as its volume) in the ratio of $x : x + y$. But by this expansion of the gases A and B, the elasticity of the gaseous mixture is diminished in such proportion that

it is reduced to x: the elasticity of the gas A therefore becomes $\left(x + y : x = x : \frac{x^2}{x+y}\right) = \frac{x^2}{x+y}$, and that of the gas B $\left(x + y : x = y : \frac{xy}{x+y}\right) = \frac{xy}{x+y}$. With this the further expansion ceases, supposing that no portion of the substance B remains unvaporized. If however this be the case, then—since the space has become larger—a fresh quantity of B is converted into gas, and the gas B regains the elasticity $= y$: and since by this action the elasticity of the gas and therefore also its expansion increases, the formation of gas and the expansion of the gaseous mixture go on till—as Dalton has shown—the volume of the gaseous mixture is to the original volume of the gas A as $x : x - y$. For since in this gaseous mixture, after its complete expansion under the pressure x, the gas B has an elasticity $= y$, that of the gas A must be only $x - y$, in order that the elasticity of the gaseous mixture may exactly balance the external pressure x.

Examples in which the preceding table of the elasticity of gases is made use of:—If at a temperature of 25° C. and under a pressure corresponding to 336 Par. lines, water be introduced in excess into a vessel containing one measure of dry atmospheric enclosed by mercury, then—supposing that the mercury stands at the same level within and without the vessel, and that the atmospheric pressure remains constant,—one measure of air will, by taking up vapour of water (since the tension of vapour of water at 25° C. or 20° R. is equal to 10·08 lines), be expanded in the ratio of 336 — 10·08 : 336 = 325·92 : 336. When alcohol evaporates in dry air at 0° C. and under a pressure of 30 English inches, the volume is increased in the ratio of 30 — 0·4 : 30 = 29·6 : 30; and in the case of ether at 0° C. the expansion is as 30 — 6·2 : 30 = 23·8 : 30.

b. The affinity of Heat for the Ponderable Substance must be superior to all other forces acting upon the same.

α. To the Cohesion of the Ponderable Substance.

Since a body introduced into a space devoid of air fills that space with a quantity of gas corresponding to the temperature—since this quantity, though it decreases with the temperature, cannot be reduced to nothing excepting at the absolute zero—since all substances, at least at high temperatures, are visibly converted into gas, and must therefore afford some, although perhaps but a small quantity at low temperatures—finally, since this formation of gas takes place in a space filled with air in the same quantity as in vacuo, only with less rapidity,—it may be concluded that of every substance situated on the surface of the earth, a certain, though perhaps extremely small portion must be converted into gas. That no diminution of weight can however be observed in pieces of metal, &c. even after many years, may result either from this circumstance, that at a certain temperature considerably below the boiling point, the cohesion and gravitation of the ponderable substance may overcome its affinity for heat—which indeed is Faraday's view (*Ann. Phil.* 28, 436; also *Pogg.* 9, 1); or possibly from this,—that when once the several bodies on the earth's surface have introduced into the atmosphere certain portions of their gases or vapours corresponding to the existing temperature, these gases may exert a pressure on the remaining matter sufficient to

prevent its further vaporization—the fluctuations of temperature on the surface of our earth being perhaps too small, in comparison with the wide interval between the ordinary temperatures of solid bodies and their boiling points, to cause any sensible condensation of these gases when the atmosphere cools, or to give rise to fresh formations of the same gases when a rise of temperature takes place,—unless perhaps many meteoric phenomena may be due to some such cause.

Ice evaporates in vacuo at temperatures below −40°, sulphuric ether at −51°, at which temperature it is solid (Configliacchi), sulphuret of carbon at −62. (Marcet.) The Torricellian vacuum is in reality filled with vapour of mercury. In the open air ice evaporates far below 0°, mercury at + 15·5°, but not at −6·7° (Faraday); oil of vitriol does not evaporate at ordinary temperatures. (Bellami, *Pogg.* 9, 7.)—By enclosing two substances in a flask filled with air, keeping them separate from one another, the one in the solid form, the other in the state of aqueous solution, and exposing the flask for four years to the ordinary temperature of the air, the following results are obtained: Crystallized oxalic acid and crystallized oxalate of ammonia evaporate over in small quantities towards aqueous solution of chloride of calcium; also protochloride of mercury towards aqueous solution of chloride of calcium; also protochloride of mercury towards aqueous solution of potash, and nitrate of ammonia in minute quantity to dilute sulphuric acid. The following on the contrary do not volatilize: sal-ammoniac or common salt towards dilute sulphuric acid; arsenious acid or calomel to caustic potash; aqueous solution of iodide of potassium to chloride of lead; common salt dissolved in water to crystallized nitrate of silver; sulphate of soda dissolved in water to crystallized hydrated chloride of barium; aqueous solution of chloride of calcium to carbonate of soda; and aqueous solution of sulphate of copper or persulphate of iron to hydrated ferrocyanide of potassium. In most of these cases, water evaporates over to the solid body and dissolves it; but the solution does not mix with that of the salt previously dissolved in water. (Faraday, *J. of Roy. Inst.* 1, 70; also *Pogg.* 19, 545.)

β. *To the Affinity of the volatile Substance for any other less volatile body with which it may be combined.*

Substances which from their own nature have a strong tendency to assume the gaseous form, so that when separated from other bodies, they exist for the most part only in the state of gas,—often, when combined with other bodies, either become wholly incapable of passing into the gaseous condition, or undergo that change only at high temperatures, because the affinity of the other body acts in opposition to that of heat.

Oxygen in red oxide of mercury, peroxide of manganese, and other metallic oxides requires a red heat to convert it into gas: so also does carbonic acid when combined with lime and other oxides of metals. Most metallic oxides do not part with their oxygen even at the highest temperatures, but are partly converted into vapour before reduction and condense again to the state of solid oxide in the cold.

Water, which when pure, boils at 100° exhibits a much higher boiling point when combined with salts, sulphuric acid, phosphoric acid and other less volatile substances.

The following table gives the boiling points of various aqueous solutions according to Faraday (*Ann. Chim. Phys.* 20, 324) and Griffiths (*Qu. J. of Sc.* 18, 90; also *Pogg.* 2. 227).—Column A contains the names of the

salts; B the quantity of dry salt in 100 parts of the solution (an *x* denotes that the quantity has not been determined); C shows the boiling point of the solution; D the name of the observer (F = Faraday, G = Griffiths).

A	B	C	D	A	B	C	D
Glauber's salt	31·5	100·6° C.	G	Borax.....	52·5	105·6	G
Corrosive sublimate	*x*	101·1	G	Bisulphate of potash..	*x*	105·6	G
Cyanide of mercury	35	101·1	G	Sulphate of magnesia	57·5	105·6	G
Cryst. verdigris....	16·5	101·1	G	Common salt.....	30	106·7	G
Cream of tartar....	9·5	101·1	G	,, ,, ...	sat.	109·0	F
Nitrate of baryta ..	26·5	101·1	G	Nitrate of strontia....	53	106·7	G
Sulphate of potash	17·5	101·7	G	Neutral tartrate of potash	68	112·2	G
Acetate of lead	41·5	101·7	G	,, ,, ,,	sat.	116·7	F
Nitrate of lead	52·5	102·3	G	Oxalic acid	sat.	112·2	G
Green vitriol	64	102·3	G	Sulphate of nickel....	65	112·6	G
Blue vitriol	45	102·3	G	Sal-ammoniac	50	113·3	G
Sulphate of copper and potash	40	102·8	G	,, ...	sat.	114·4	F
Boracic acid	*x*	103·3	G	Nitrate of potash	74	114·4	G
Chlorate of potash..	40	103·3	G	,, ,, ...	sat.	115·6	F
Ferrocyan. potassium	55	103·3	G	Rochelle salt.....	90	115·6	G
Oxalate of ammonia	29	103·3	G	Nitrate of soda	60	119·0	G
Carbonate of soda ..	*x*	104·4	G	Acetate of soda	60	124·4	G
Chloride of barium	45	104·4	G	Carb. potash .... sat.	about	140·0	F
Alum	52	104·4	G	Potash..... sat.		157·8	G
Sulphate of zinc....	45	104·4	G	Nitrat. ammonia.. sat:		182·2	G
Oxalate of potash ..	40	104·4	G	Soda ....sat.		215·5	G
Phosphate of soda..	*x*	105·6	G				

Boiling points of aqueous solutions according to Legrand (*Ann. Chim. Phys.* 59, 423; also *J. pr. Chim.* 6, 56.)—The following table gives the number of parts of each salt dissolved in 100 parts of water: in the first column on the left is given the boiling point corresponding to this proportion. Nitrate of ammonia was employed in the crystallized state, and common phosphate of soda in as dry a state as possible (but not ignited); the other salts in the perfectly anhydrous condition; *a* is chloride of calcium, *b* acetate of potash, *c* nitrate of ammonia, *d* nitrate of lime, *e* simple carbonate of potash, *f* acetate of soda, *g* nitrate of soda, *h* chloride of strontium, *i* nitrate of potash, *k* sal-ammoniac, *l* neutral tartrate of potash, *m* chlorate of potash, *n* common salt, *o* chloride of potassium, *p* ordinary phosphate of soda, *q* simple carbonate of soda, *r* chloride of barium. The number under a horizontal stroke gives the boiling point of the saturated solution. This table has a practical value: for by means of it, the quantity of salt in any solution may be found from its boiling point.

Boiling Point.	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
101°	10·0	10.5	10·0	15·0	13·0	9·9	9·3	16·7	12·2
102	16·5	20·0	20·5	25·3	22·5	17·6	18·7	25·2	26·4
103	21·6	28·6	31·3	34·4	31·0	24·1	28·2	32·1	42·2
104	25·8	36·4	42·4	42·6	38·8	30·5	37·9	37·9	59 6
105	29·4	43·4	53·8	50·4	46·1	36·7	47·7	43·4	78·3
106	32·6	49·8	65·4	57·8	53·1	42·9	57·6	48·8	98·2
107	35·6	55·8	77·3	64·9	59·6	49·3	67·7	54·0	119·0
108	38·5	61·6	89·4	71·8	65·9	55·8	77·9	59·0	140·6
109	41·3	67·4	101·9	78·6	71·9	62·4	88·3	63·9	163·0

Boiling Point.	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
110°	44·0	73·3	114·9	85.0	77·6	69·2	98·8	68·9	185·9
111	46·8	79·3	128·4	91·9	83·0	76·2	109·5	74·1	209·2
112	49·7	85·3	142·4	98·4	88·2	83·4	120·3	79·6	233·0
113	52·8	91·4	156·9	104·8	93·2	90·9	131·3	85·3	257·6
114	55·6	97·6	172·0	111·2	98·0	98·8	142·4	91·2	283·3
115	58·6	103·9	188·0	117·5	102·8	107·1	153·7	97·5	310·2
116	61·6	110·3	204·4	123·8	107·5	115·8	165·2	104·0	115·9°:
117	64·6	116·8	221·4	130·0	112·3	125·1	176·8	110·9	335·1
118	67·6	123·4	238·8	136·1	117·1	134·9	188·6	117·8°:	
119	70·6	130·1	256·8	142·1	122·0	145·2	200·5	117·5	
120	73·6	136·9	275·3	148·1	127·0	156·1	212·6		
122	79·8	150·8	314·0	160·1	137·0	175·3	121°:		
124	86·2	165·1	354·0	172·2	147·1	204·5	224·8		
126	98·2	180·1	396·0	184.5	157·3	124·4°			
128	92·4	196·1	440·2	197·0	167·7	209·0			
130	104·6	213·0	487·4	209·5	178·1				
132	110·9	230·6	537·3	222·2	188·8				
136	123·5	267·5	645·0	248·1	135°:				
140	136·3	308·3	770·5	274·7	205·0				
144	149·4	354·9	915·5	302·6					
148	163·2	407·9	1081·5	333·2					
152	178·1	467·6	1273	151°					
156	194·3	534·1	1504	362·2					
160	212·1	607·4	1775						
164	231·5	687·6	2084						
168	252·8	775·0							
172	276·1	169°:							
176	301·4	798·2							
179·5	325·0								

Boiling Point.	*k*	*l*	*m*	Boiling Point.	*n*	*o*	*p*	*q*	*r*
101°	7·8	26·9	14·64	100·5°	4·4	4·7	11·0	7·5	11·0
102	13·9	47·2	29·28	101	7·7	9·0	21·0	14·4	19·6
103	19·7	65·0	43·92	101·5	10·8	13·2	31·0	20·8	26·2
104	25·2	82·3	58·56	102	13·4	7·1	40·8	26·7	32·5
				102·5	15·9	20·9	50·3	32·0	38·6
105	30·5	100·1	104·20:	103	18·3	24·5	59·4	36·8	44·5
106	35·7	118·5	61·5	103·5	20·7	28·0	68·1	41·0	50·3
107	41·3	137·3		104	23·1	31·4	76·4	44·7	56·0
108	47·3	156·5						47·9	
109	53·5	176·1		104·5	25·5	34·6	84·2		104·4°:
110	59·9	196·2						104·6°:	60·1
111	66·4	216·8		105	27·7	37·8	91·5	48·5	
112	73·3	237·9		106	31·8	44·2	105·0		
113	80·8	259·5							
114	88·1	281·6		107	35·8	50·5	106·6°:		
				108	39·7	56·9	111·6		
115	114·2°:	114·7		108·4	40·2	59·4			
116	88·9	296·2							

In a similar manner, the boiling point of alcohol is raised by mixing it with water, and that of ether by mixing it with alcohol. (*Comp.* Magnus, *Pogg.* 38, 487.)—In like manner, permanent gases combined with water and other liquids require an elevation temperature or diminution of pressure make them escape. In this action an anomaly is observed proceeding from a kind of sluggishness (like that described pp. 9—12), viz., that the gases do not escape at once in the quantities which might be expected under the given circumstances, but that their escape is favoured by agitation or by the immersion of solid bodies, particularly of such as have sharp angles, *e. g.*, glass rods, wires, metallic filings, silver leaf, sand, sugar-dust. The formation of gas-bubbles appears always to proceed from the solid bodies and from the sides of the vessel, and never from the interior of the liquid, as if the contact of a solid body were essential to the formation of gas. Many solid bodies may however act by means of air adhering to them, which is either itself absorbed by the liquid and drives out the other gas, or else supplies the first bubbles, which then increase in volume by attracting the other gas. (*Compare* Oerstedt, *N. Gehl.* 1, 227; Liebig, *Ann. Pharm.* 30, 13; Schönbein, *Pogg.* 40, 382.)

Evaporation, *Drying*, or *Desiccation*, and in many cases *Calcination*, *Roasting*, or *Torrefaction* are operations the object of which is, for the most part, the separation of a more volatile (in the case of evaporation and drying it is a liquid) from a less volatile substance. That these operations proceed most quickly in vacuo will be understood from that which immediately follows.

B. Phenomena accompanying Vaporization.

a. Time in which it takes place.

The rapidity of vaporization is greater, the stronger the affinity of the ponderable body for heat, the higher the temperature, and the less the resistance which the surrounding envelope offers to the expansion of the gas.

In a vacuum vaporization takes place almost instantaneously, whatever may be the nature of the substance: water boils in vacuo at 20°; in so far however as heat is necessary to the production of vapour, the vaporization of the body may be retarded as its temperature gets lower. In a space filled with air or any other gas, vaporization cannot take place instantaneously, unless the substance is capable of producing vapour of great elasticity at the given temperature, and sufficient heat is present for the production of that vapour. Liquid carbonic acid vaporizes almost instantly in the air, to within about $\frac{1}{8}$ of the whole, which solidifies (so that according to Thilorier, 1 gramme of this liquid produces on opening the vessel an explosion as violent as that of 1 gramme of gunpowder); but 346 grains of solid carbonic acid exposed to the air at + 25° lose only 3 or 4 grains per minute, and do not wholly disappear in less than 3½ hours (still more slowly when wrapped up in cotton.) (Mitchell.)—The liquid acid already indeed contains a large portion of the heat of fluidity required for its conversion into vapour, and moreover contains a larger quantity of sensible heat, inasmuch as it takes the temperature of the vessels in which it is enclosed,—the solid acid on the contrary must take all its heat from the surrounding bodies. All explosions, detonations, and fulminations arise from a sudden formation of gas brought about by great affinity for heat

and a high temperature, the resistance of the surrounding envelope being completely overpowered. Since nitrogen, when it separates from its combinations and assumes the gaseous state, produces the most fearful explosions, even when no great rise of temperature takes place (*e. g.*, in the decomposition of chloride of nitrogen) a peculiarly great affinity for heat must be ascribed to it.

If on the other hand the tension of the nascent vapour is less than the pressure of the external air, so that the vaporization can only proceed by means of the adhesion of the existing gas to that which is in course of formation, then—since the portion of air which is in contact with the vaporizing body can only be charged with the nascent vapour in the same proportion as a vacuum—the rate of evaporation will be determined by the rapidity with which the particles of the existing gas are renewed on the surface of the vaporizing body, and will therefore be very slow in a state of rest, but quicker in proportion to the facility with which the existing gas is renewed.

b. Situation in which the formation of Gas or Vapour takes place.

The vaporization of a body takes place in that particular part in which the conditions of vaporization are completely fulfilled.

If a body is very volatile and contains a quantity of heat sufficient to convert it into gas, it instantly assumes the gaseous form throughout its whole mass, as soon as the external pressure allows of such a change. Liquid carbonic acid, sulphuretted hydrogen, and chlorine are instantaneously converted into gas with a kind of explosion, as soon as the vessels containing them are opened.

When a less volatile body is heated from without to increase its tendency to assume the gaseous form, the formation of vapour takes place principally at that part where the heat enters; and when the heating takes place, not from above but from the bottom and sides, and the heated body is liquid, the vapour as it is produced rises in bubbles through the liquid and produces the phenomenon of *Boiling* or *Ebullition*. These bubbles of vapour have the peculiar property of being almost always evolved from the surfaces of solid bodies, either the sides of the vessels or bodies floating in the liquid:—the edges and angles of such bodies present peculiar facilities for the evolution of gas.

When vaporization takes place only from the surface of a body, either because the heat has access to that part, or because the evolution of gas takes place through the medium of a gas already present, the action can only be recognized by the diminution in bulk of the body; it is then called *Evaporation*.

c. Absorption of Heat.

As in liquefaction, so likewise in the formation of gas or vapour, the heat which enters into combination with ponderable bodies passes into a state in which it is insensible to the feelings and to the thermometer. Any given substance absorbs the same quantity of heat to form gas or vapour of a given density, whether the vaporization takes place quickly in vacuo or more slowly in a space previously filled with another gas; in the latter case however the reduction of temperature is never so great as in the former, because the heat has more time to enter from without and supply the place of that which has become latent,—and secondly, because the other gas already present gives up a portion of its free heat to that which is being formed—an effect which cannot take place in vacuo.

Solid carbonic acid produces in vacuo, when the external temperature is 30°, a cold of —93·3°; a pasty mixture of the same with alcohol reduces the temperature to — 92°, and with ether to — 99°. (Mitchell.)—Cotton moistened with sulphuret of carbon and wrapped round a thermometer lowers it in vacuo from + 16° to — 62°. (Marcet.) Liquid sulphurous acid produces in vacuo a temperature of — 60°. (De la Rive, *Pogg.* 15, 526.) 20 grammes of mercury placed in a watch-glass under the receiver of an air-pump in contact with an equal quantity of liquid sulphurous acid freezes in five minutes. (Bussy.)—If the formation of gas in a space devoid of air be continually renewed by the introduction of a substance which will unite with the vaporized body and form a non-gaseous compound, great degrees of cold may be produced even with substances which are not very volatile. Water placed in a capsule near a basin of oil of vitriol in a vacuum is soon converted into ice; well dried powder of trap-porphyry or oatmeal will produce the same effect as oil of vitriol. (Leslie.)—At a temperature of + 15°, Configliachi produced,—by surrounding a thermometer with cotton moistened with various liquids and introducing it into a vacuum in which there was also a vessel containing oil of vitriol,—with water a temperature of — 41·25°, with sulphuric ether — 51°, with alcohol, —37·5°, with nitric ether, — 31·25°, and with hydrochloric ether, — 30°. In the same manner, Graham (*Schw.* 55, 188) obtained with water a temperature of —14°, and with alcohol (or a mixture of 3 parts alcohol with one part water, which acts equally well because the water renders latent a larger quantity of heat), a temperature of —31°. (*Comp.* Dove, *Pogg.* 19, 318.)

Wollaston's *Cryophorus* (*Ann. Phil.* 2, 230; also *Gilb.* 52, 274) consists of two glass bulbs connected by a tube,—exhausted of air and containing a little water. If all the water be made to pass into one of the bulbs, and the empty bulb immersed in a freezing mixture so as to congeal the vapour contained in it, the water in the other bulb will be frozen in consequence of the rapid evaporation which ensues.—Perkin's apparatus for cooling water for household uses by the evaporation of ether, in such a manner that the ether is not lost, acts on similar principles. (*Ann. Pharm.* 22, 214.)

On opening the stop-cock of an iron vessel containing liquid carbonic acid and directing the stream of vaporizing acid by means of a narrow tube into a hollow sphere, the latter quickly becomes filled with carbonic acid solidified like flakes of snow, the temperature falling to — 100°. The stream directed on the bulb of a spirit-thermometer cools it to — 90°; but it will not freeze more than a small quantity of mercury, whereas the stream of gas produced by a mixture of carbonic acid and ether soon freezes 50 grammes. (Thilorier.) When the liquid carbonic acid is enclosed in a strong glass tube closed with a brass cock and tube, a violent motion of the liquid is observed on opening the stop-cock, $\frac{1}{8}$ of the carbonic acid remains frozen in a dense but yet porous mass, and exhibits at the moment of freezing a temperature of — 65°. (Mitchell.)

When a body passes to the gaseous state in a space already filled with another gas, and at a temperature at which the tension of the gas in process of formation is less than that already existing, the cold produced is greater—the stronger the tendency of the substance to assume the gaseous form—the greater the quantity of heat required for its conversion—the greater the rarefaction of the existing gas,—the smaller the quantity of the other gas already contained in it (if it be already saturated, no farther

vaporization and therefore no further cooling can take place)—and the more it is set in motion.

When vaporization takes place in the open air below the boiling point, the maximum of cooling is produced, as soon as the quantity of heat rendered latent by the process becomes equal to that which the air gives up in order to place itself in equilibrio, as regards pressure and temperature, with the gas in course of formation, + the quantity supplied from without (this however may be neglected when the difference does not exceed a few degrees). Gay-Lussac's formula for calculating the lowest temperature attainable in this manner will be found in the *Ann. Chim. Phys.* 21, 82.—If air dried by chloride of calcium under a pressure of 0·76 metre be directed on a thermometer bulb surrounded with baptist, and the baptist be moistened with water, the following degrees of cold will be produced:

at	Cooling of	at	Cooling of	at	Cooling of
0°	5·82°	9° C.	8·61°	18° C.	11·96°
1	6·09	10	8·97	19	12·34
2	6·37	11	9·37	20	12·73
3	6·66	12	9·70	21	13·12
4	6·96	13	10·07	22	13·51
5	7·27	14	10·44	23	13·90
6	7·59	15	10·82	24	14·30
7	7·92	16	11·20	25	14·70
8	8·26	17	11·58		

When the external pressure to which the air is subjected amounts to only 0·65 metre, a cooling of 10·5° takes place at 12·5°, and at 0·5 metre it amounts to 12° at the same temperature. According to the preceding table, dry atmospheric air would cause the freezing of water at 8°; but since common air contains a large quantity of vapour of water, the freezing of water usually commences at about 2°: it is only on high mountains, where the air is dryer and rarer, that congelation takes place at higher temperatures. (Gay-Lussac.)—A wet finger exposed to the air becomes coldest on the side from which the wind blows.—*Alkaraza*, a porous water-jug in which the water which exudes through the pores evaporates and thus cools that which remains.—The production of ice in India (*Crell. Chem. J.* 1, 197) is according to Wells (*Schw.* 22, 187) and D. Scott (*Edinb. J. of Sc.* 8, 216; also *Schw.* 52, 372) an effect not so much of cooling by evaporation, as of radiation towards empty space the temperature of which is very low.

The Psychrometer of August (*Pogg.* 5, 69 and 335; 14, 139) is an instrument for determining the hygrometric state of the atmosphere. Two small thermometers *a*, *b*, are placed near one another, one of them *b* being covered with wet muslin: its temperature becomes lower than that of *a*, in proportion as the air is drier and more water evaporates. The difference of the temperatures indicated by *a* and *b* being multiplied by 2, and the product subtracted from the temperature denoted by *a*, the remainder shows the temperature at which the aqueous vapour in the air will condense.

If a thin glass bulb containing water be surrounded with cotton, ether dropped on the cotton and a stream of air directed on it, the water will freeze in a few minutes. If the bulb of a mercurial thermometer be wrapped up in cotton, then liquid sulphurous acid dropped on the

cotton and the instrument moved about in the air, the mercury gradually sinks to — 36°, then falls suddenly into the bulb and freezes. (Bussy, *J. Pharm.* 10, 202; also *Schw.* 41, 451.) Half an ounce of mercury placed in a watch-glass and covered with liquid sulphurous acid, freezes when blown upon with a pair of bellows. (Wach, *Schw.* 50, 24.) Solid carbonic acid moved about in the air produces a degree of cold amounting to —72·2°; if it be mixed with ether the temperature falls to — 76·7°; on blowing on the mixture it is further reduced to — 79°. Mercury immersed in solid carbonic acid in the open air freezes in a few seconds; in a mixture of solid carbonic acid and ether, it freezes instantly. Liquid carbonic acid enclosed in a tube may also be solidified by immersion in such a mixture; the frozen portion sinks to the bottom of that which still remains liquid, till the whole becomes frozen into a compact mass like that usually formed by solid carbonic acid. (Mitchell.)

When a body is heated in the air to its boiling point, its temperature cannot be raised higher by any further addition of heat, because all the heat which afterwards enters the body combines with it to form a gas and thus becomes latent. The vaporizing body remains constantly at the boiling temperature, and the vapour produced has likewise the same temperature, provided no more heat be subsequently added to it. This is the principle of the *Water-bath*, *Balneum Maris s. Mariae*, a covered vessel in which water is heated to the boiling point: the cover has apertures in it, into which a number of vessels are inserted so as to dip either into the water or into the steam; they are thus exposed to a uniform temperature not exceeding 100°. If a lower temperature be required, spirit of wine of various strengths may be used; higher temperatures may be obtained by means of solutions of chloride of calcium of various degrees of concentration.

Variations in the temperature of a body heated to ebullition may be produced by the following causes.

1. By change of atmospheric pressure.

Par. inches..	26	26·5	27	27·5	28	28·5	29
Boiling point	98·366°	98·775°	99·183°	99·592°	100	100·408°	100·87°

Hence the difference for each inch is about 0·817°. (Graham.)

2. If heat be applied to the lower part of a liquid, such as water, contained in a deep vessel, the heat must rise to a higher degree at this lower part before bubbles of vapour can be developed,—because their elastic force has to overcome, not only the atmospheric pressure, but likewise that of the superincumbent column of liquid. Under a column of water 10 metres high (= 1 atmosphere) water cannot boil below 122°; but in passing up through the liquid, the vapour expands and becomes cooler, so that when it escapes at the surface it has a temperature of 100°. (Gay-Lussac.)

3. Since the formation of gas in a mass of liquid takes place principally at the edges of any solid bodies which may be contained in it, it follows that, when no such edges are present, the heat must accumulate in somewhat greater quantity before the bubbles can form; hence the boiling point of a liquid, *e. g.* water, is lower by some tenths of a degree, 1½° at most, and the boiling goes on more uniformly and less by fits and starts, when the surface of the vessel is uneven, or when metallic powders, filings, or wire are introduced, or when the liquid is agitated. (Achard, *Schw.* 27, 27;—Gay-Lussac, *Ann. Chim.* 82, 174; *Ann. Chim. Phys.* 7, 307:—Muncke, *Gilb.* 57, 215.) Water boils in metallic vessels at

100°, in glass vessels at 101·33°; but in the latter case, the vapour which rises has a temperature of only 100°, the higher boiling point being probably due to a greater adhesion of glass to water. (Rudberg, *Pogg.* 40, 49.) Ether of 0·755 sp. gr. which boiled at 44·4° C. in a glass flask, required a heat of 65·5°, and sometimes even 79°, to make it boil in a glass tube closed at the bottom and immersed in hot water (in the latter case it could not move so freely); metallic filings or wire, fragments of glass, or pounded glass lowered the boiling point to 51°; if the liquid had ceased to boil at this temperature, the ebullition was reproduced on the introduction of shavings or splinters of wood, (these however must likewise have acted by means of the air which escaped from their pores. *Gm.*) Similar results were obtained with alcohol and water. (Bostock, *Ann. Phil.* 25, 196.) Watery liquids heated to the boiling point and then removed from the fire, exhibit fresh ebullition on the introduction of solid bodies, only when a permanent gas likewise comes into play,—because the mixture of watery vapour and permanent gas sustains the pressure of the atmosphere at a temperature below 100°. Pure boiled water evolves no bubbles of vapour on the introduction of platinum wire, but nevertheless boils up: so also does pure water which still contains air, on the immersion of a platinum wire which has been freed from adhering air by previous boiling. The same phenomenon is exhibited by water freed from air on the introduction of a metal wire having air still adhering to it; and more violently on the introduction of a piece of wood; also by water containing from $\frac{1}{1000}$ to $\frac{1}{100}$ of sulphuric or other acids, on the immersion of iron or other metals which develope gas by the action of the acid, or on the introduction of calcspar. (Schönbein, *Pogg.* 40, 391.)

4. Many foreign bodies produce precisely the opposite effect on the boiling point of a liquid: they cause an accumulation of heat in the liquid, and thus raise the temperature far above the boiling point,—till on a sudden, this excess of heat is expended in the formation of vapour, which not only causes a rising and projection of the liquid, but also occasions violent noisy agitation and often fracture of the containing vessel. Upon this, the liquid goes on boiling but with continually diminishing force; and at length comes to rest and remains tranquil, till a fresh accumulation of heat causes the same action to be repeated. This *jumping ebullition* occurs in water containing sulphate of potash in greater quantity than it is able to dissolve, in oil of vitriol which contains even a small quantity of sulphate of lead in the state of powder, and in nitric acid containing crystals of nitrate of silver. The presence of fat oil, according to Scrymgeon, raises the boiling point of water some degrees; and, according to Magnus, a layer of volatile oil on the surface of water causes a rise of temperature of 10° above the boiling point, accompanied by violent, percussive ebullition, which however passes into quiet boiling as soon as the layer of oil becomes broken by bubbles of vapour. Water holding salts in solution,—*e. g.* neutral tartrate of potash, and more especially caustic potash—has a great tendency to become overcharged with heat, so that the liquid flows over when stirred. The presence of metal filings, wire, or cuttings tends to prevent irregular ebullition, inasmuch as metallic points facilitate the formation of bubbles; but according to Legrand (*Ann. Chim. Phys.* 59, 426), platinum is not nearly so efficacious as zinc or iron, metals in fact which decompose water,—although the zinc placed in saline solutions, under such circumstances, is not sensibly diminished but only slightly tarnished.

When a volatile body has its boiling point raised by combination with a less volatile substance, the vapour at the moment of its formation likewise possesses the higher temperature, but quickly cools down to the ordinary boiling point of the body: *e. g.* vapour of water evolved from boiling saline solutions. (Gay-Lussac, *Ann. Chim. Phys.* 20, 324; 70, 420.) —Pambour, *Jahresb.* 19, 55.) According to Faraday (*Ann. Chim. Phys.* 20, 325) and Rudberg (*Pogg.* 34, 257) the vapour of water evolved from boiling saline solutions, even from a solution of chloride of calcium which boils at 150°, has always the temperature of 100°.

When a volatile liquid is situated at the bottom of a less volatile one with which it does not mix, its boiling point is somewhat raised in proportion to the pressure exerted by the upper liquid; but the temperature of the vapour bubbles which rise from the lower through the upper liquid is below the boiling point of the more volatile body, because its vaponr becomes mixed to a certain extent with that of the upper liquid (the temperature of which is somewhat higher than that of the lower)—so that the mixed vapour, by virtue of the sum of its tensions, is able to balance the pressure of the air at a somewhat lower temperature. Thus, the boiling point of sulphuret of carbon situated below a layer of water is 47°, and the temperature of the mixed vapour 43·5°; the temperature of water boiling under oil of turpentine is 102°, and that of the mixed vapour 94·5°. A volatile liquid, situated above a less volatile one, *e. g.* water above mercury, boils at the same temperature as when alone. (Magnus, *Pogg.* 38, 481.) *Comp.* Liebig (*Pogg.* 24, 277)—Gay-Lussac (*Ann. Chim. Pys.* 49, 393; 50, 111).

Leidenfrost's Experiment. When a volatile liquid is dropped on a surface heated to redness or a little below, it does not adhere to the surface, but swims upon it in a globular form: neither does it become heated to its boiling point; but diminishes slowly in consequence of the formation of vapour, which escapes between the heated surface and the liquid, and likewise—when the quantity of liquid is considerable—escapes in bubbles through it. When the temperature of the surface falls to a certain point, the liquid comes in contact with it, boils with violence, and is rapidly converted into vapour. The surface may consist of platinum, silver, copper, iron, and other metals, or of glass or porcelain; but the lower its conducting power, the more strongly must it be heated. The experiment succeeds with sulphurous acid, ether, alcohol, water, oil of vitriol, and mercury; the higher the boiling-point of the liquid, the more strongly must the surface be heated. A small platinum crucible, strongly ignited over an Argand spirit-lamp, may be gradually filled with water to the brim. Melted slags falling in drops upon water swim for some time on the surface in a state of incandescence, and then sink with a hissing noise. (Faraday.) Alcohol dropped on an almost boiling mixture of alcohol and oil of vitriol, swims upon it in globules. Potash and its salts, likewise charcoal powder or ink, added to the water, interfere with the phenomenon, according to Pouillet. The same appearance is presented, according to Delatre & Boutigny, by sulphurous acid, water, and ether, even in vacuo. If, on the other hand, a heated glass flask containing ether in this peculiar floating condition be stopped with the finger, and the formation of vapour thereby prevented, the phenomenon will be arrested. (Desmarest.) Liquids in this state are not resolved into permanent gases, but evaporate unchanged. On connecting the metallic surface with one pole of a simple galvanic circle, and the liquid with the other, it is found, according to Poggendorff, that no electric current passes,—and

consequently, the liquid and the heated surface are not in contact.—The heat which radiates from the heated surface undoubtedly produces, before the surface and the liquid can come into immediate contact, a quantity of vapour sufficient to support the liquid; and this vapour being continually renewed prevents the liquid from touching the surface, and thus intercepts the more rapid transmission of heat by conduction. [*Compare* Eller (*Hist. de l'Acad. de Berl.* 1746, 42), who appears to have been the first to observe the effect; Leidenfrost (*De aquæ comm. qualitatibus. Duisb.* 1756); Klaproth (*Scher. J.* 7, 646); Muncke (*Pogg.* 19, 514); Faraday (*Qu. J. of Sc. N. S.* 3, 221); Buff (*Pogg.* 25, 591; also *Ann. Pharm.* 2, 220); Lechevallier (*J. Pharm.* 16, 666); Baudrimont (*Ann. Chim. Phys.* 61, 319); Laurent (*Ann. Chim. Phys.* 62, 327); Boutigny (*Pogg.* 51, 130); Ensmann (*Pogg.* 51, 444); Ritter (*J. pr. Chem.* 10, 108); Desmarest (*J. Pharm.* 26, 746); Poggendorff (*Pogg.* 52, 538).]

The statement of Jaquemyns (*Pogg.* 37, 467), that the bottom of a metallic vessel may be touched with impunity as long as water is boiling in it, deserves verification.

When a volatile body is exposed to a high temperature in a narrow space, either vacuous or filled with air, and enclosed by solid walls, the vapour produced from it acquires a continually increasing elasticity, and thus raises the temperature of the body more and more,—so that at length a degree of heat is attained at which the body, under the ordinary temperature of the air, would be instantly converted into vapour. (*Papin's Digester.*)

¶ Faraday has succeeded in freezing mercury in a red-hot platinum crucible, by putting into the crucible, first ether, then solid carbonic acid, and then—when the whole is in the spheroidal state—dipping into it a small metal spoon containing between 400 and 500 grains of mercury. The mercury freezes in two or three seconds. (*N. Ann. Chim. Phys.* 19, 383.) The film of vapour which intervenes between the red-hot metal and the semi-fluid mass of ether and carbonic acid, completely prevents the communication of heat from the crucible to the mercury.—In a similar manner, water may be frozen in a red-hot crucible by the agency of liquid sulphurous acid. ¶

d. Increase of Volume.

The expansion of a body on passing into the gaseous state varies according to its nature, and likewise according to temperature and external pressure.

One measure of water at 0° yields, under a pressure of 0·76 metre, 1700 measures of vapour at 100°, according to Gay-Lussac, and 1728 according to Dalton: 1728 is the cube of 12; hence, according to Dalton's view, the atoms of water in the gaseous state must be removed from one another 12 times as far as in the liquid state; if, however, there be any foundation for this supposition, it must be true for all external pressures. (On the expansion of certain other bodies by conversion into gas, *comp.* pp. 57, 3, and 73, 1.)

From the following table, Gay-Lussac concludes (*Ann. Chim. Phys.* 2, 130) that bodies, in assuming the gaseous form, expand so much the less in proportion as they suffer a greater amount of contraction in cooling from their boiling points:—

	Water.	Alcohol.	Sulphuret of Carbon.	Eth
Contraction of 1000 measures of liquid when cooled from the boiling point to a temperature 50° below it	28·56	56·02	56·28	72·
Quantity of vapour at 100° (in litres) produced by 1 gramme of liquid	1·700	0·661	0·402	0·
Measures of vapour at 100° produced by 1 measure of liquid at the boiling point	1633·1	488·3	491·1	285·

Specific Gravity of Inorganic Gases.

	Specific Gravity, that of Air = 1·0000.						Weight in gramm 1 Litre of Gas at Bar. 0·76 met	
	of H = 1	Calculation.	Observation.				Calculation.	Observa
O.....	16	1·1093	1·087 F S	1·088 A P	1 1026 B D		1·4410	1·4323 B D
			1·103 K	1·1031 Bf	1·1036 B A			1·4337 B A
			1·1056 S	1·1057 D B	1·1117 To			
			1·128 H D					
H.....	1	0·0693	0·0688 B D	0·0693 To	0·0732 B A		0·0901	0·0894 B D
			0 0769 L	0·092 Ca				
HO.....	9	0·6239	0·6235 G	0·625 Dz	0·6896 Tr		0·8105	0·81 G
C?.....	6	0·4160					0 5404	
CO.....	14	0·9709	0·94 Da	0·9409 C D	0·9678 Cr		1·2609	1·14 C D
			0·9698 To					
CO^2.....	22	1·5252	1·4993 L	1·5191 Bf	1·5196 B A		1·9814	1·9734 Bf
			1·524 A P	1·5245 B D	1·5926 S			1·9805 B D
			1·57 Ca Da					
B?.....	10·8	0·7487					0·9726	
P.....	62·8	4·3539	4·42 Ds	4·58 Mt			5·6561	
PH^3	17·2	1·1926	1·146 Ro	1·1214 Ds	1·165 Bf		1·5493	1·5134 Bf
S.....	96	6·6556	6·5635 Ds	6·9 - Mt			8·6463	
SO^2.....	32	2·2186	2 193 H D	2·2222 To	2·2277 Bf		2·8831	2·894 Bf
			2·234 Te	2·247 Bz	2·2553 G T			
			2·263 K					
SO^3	40	2·7732	3·0 Mt				3·6027	
SH.....	17	1·1786	1·106 K	1·1791 To	1·1912 G T		1·5311	1·5475 G T
			1·1967 H D	1·236 Te				
CS^2	38	2·6345	2·6447 G	2·688 Cb			3·4225	3·4357 G
Se?	240	16 6392					21·6160	
SeO^2	56	3·8825	4·03 Mt				5·0437	
SeH.....	41	2·8425	2·795 Bi				3·6927	
.....	126	8·7356	8·716 Ds				11·3483	11·323 Ds
IH.....	63·5	4·4024	4·3757 To	4·4429 G			5·7191	5·7719 G
IH^3, IH.	40·35	2·7975	2·769 Bi				3·6342	
Br	78·4	5·4355	5·54 Mt				7·0618	
BrH.....	39 7	2·7524	1·906 Bi				3·5756	
Cl.....	35·4	2·4543	2·34 D A	2·305 H D	2·424 G		3·1884	3·2088 G
			2·47 G T	2·5 To	2·713 To			
ClO^4	33·7	2·3364					3·0352	
ClH	18·2	1·2618	1·23 Da	1·2474 B A	1·2555 Bf		1·6392	1·6205 B A
			1·278 B G	1·2844 To	1·43 Br			
COCl....	49·4	3·4249	3·4604 To	3·6808 J D			4·4493	
BCl^3	58·5	4·0558	3·942 Ds				5·2689	5·1212 Ds
PCl^3	68·8	4·7699	4·875 Ds				6·1965	6·3532 Ds
PCl^5	69·47	4·8161	4·85 Mt				6·2506	
SCl^2	67·4	4·6728	4·70 Ds	4·77 Ma			6·0704	
SO^2Cl ..	67·4	4·6728	4·665 Rg				6·0704	
F?	18·7	1·2964					1·6841	
FH?	9·85	0·6829					0·8871	

	Specific Gravity, that of Air = 1·0000.						Weight in Grammes of 1 Litre of Gas at 0°; Bar. 0·76 met.	
	of H = 1.	Calculation.	Observation.				Calculation.	Observation.
BF^3	33·42	2·3190	2·3124 Ds	2·3694 To	2·3709 JD			
N	14	0·9706	0·9426 L	0·967 HD	0·9691 BA		1·2609	1·259 B A 1·2675 B D
			0·972 DB					
			0·9729 To	0·9757 BD	0·985 K			
NO	22	1·5252	1·3629 Bt	1·5204 Co	1·5269 To		1·9814	1·9752 Co
			1·614 Da					
NO^2	15	1·0399	1·0388 Be	1·041 To	1·094 HD		1·3509	1·3495 Be
			1·1887 K					
NO^4	23	1·5946	1·72 Mt				2·0715	
NH^3	8·5	0·5893	0·5901 HD	0·5931 To	0·5967 BA		0·7655	0·7752 B A
			0·60 K	0·6022 AP				
NH^3, CO^2	13	0·9013	0·8992 Ro	0·90 Bi			1·1708	
$NH^3, 2SH$	12·74	0·8840	0·884 Bi				1·1481	
NH^3, ClH	13·38	0·9255	0·890 Bi				1·2023	
Si?	14·8	1·0261					1·3330	
$SiCl^2$	85·6	5·9347	5·939 Ds				7·7098	7·7154 Ds
SiF^2	52·2	3·6190	3·5735 JD				4·7014	
Ti?	24·5	1·6986					2·2066	
$TiCl^2$	95·3	6·6072	6·836 Ds	3·600 Ds	4·17 Da		8·5834	8·881 Ds
$CrCl^3, 2\dddot{C}r$	79·5	5·5117	5·5 Ds	5·9 W			7·1602	
As	150·4	10·4272	10·6 Mt				13·5460	
AsO^6	198·4	13·7551	13·85 Mt				17·8692	
AsH^3	39·1	2·7108	2·695 Ds				3·5216	3·5023 Ds
AsI^3	226·6	15·7102	16·1 Mt				20·4091	
$AsCl^3$	90·7	6·2882	6·3006 Ds				8·1690	8·1852 Ds
Sb?	258	17·8871					23·237 I	
$SbCl^3$	117·6	8·1532	7·8 Mo				10·5918	
Te?	384	26·6227					34·5855	
TeH	65	4·5064	4·49 Bi				5·8543	
NH^3, TeH	20·5	1·4213	1·32 Bi				1·8464	
Bi?	106·4	7·3767					9·5831	
Bi^2Cl^3? ..	158·5	10·9888	11·35 Jq				14·2755	
Sn?	59	4·0905					5·3139	
$SnCl^2$	129·8	8·9990	9·1997 Ds				11·6906	11·9514 Ds
Hg	101·4	7·0301	6·976 Ds	7·03 Mt			9·1328	9·0625 Ds
HgS	78·27	5·4262	5·51 Mt				7·0492	
HgI	227·4	15·7656	15·9 Mt				20·4811	
Hg^2Br	140·6	9·7478	10·14 Mt				12·6634	
HgBr	179·8	12·4656	12·16 Mt				16·1941	
Hg^2Cl	119·1	8·2572	8·35 Mt				10·7269	
HgCl	136·8	9·4843	9·8 Mt				12·3211	

Remarks on the preceding Table.

AP. denotes Allen & Pepys; Be. Bérard; Bf. Buff; Bi. Bineau; Br. Brisson; Bt. Berthollet; Bz. Berzelius; BA. Biot & Arago; BD. Berzelius & Dulong; BG. Biot & Gay-Lussac; Ca. Cavendish; Cb. Couerbe; Co. Colin; Cr. Cruikshanks; CD. Clement & Desormes; Da. Dalton; Dm. Deiman; Ds. Dumas; Dz. Despretz; DB. Dumas & Boussingault; FS. Fourcroy, Vauquelin, & Seguin; G. Gay-Lussac; GT. Gay-Lussac & Thénard; H. Henry; HD. Humphry Davy; JD. John Davy; Jq. Jaquelain; K. Kirwan; L. Lavoisier; Ma. Marchand; Mt. Mitscherlich; Rg. Regnault; Ro. Rose; S. Saussure; Te. Thénard; Tf. Tromsdorff; To. Thomson; Tr. Tralles; W. Walter.

The calculation of the specific gravity of gases rests upon the following suppositions: (1.) That the atomic weights of the elementary bodies are those given on page 50, and consequently, that if one measure of oxy-

gen gas weigh 16, one measure of nitrogen gas will weigh 14, and one measure of carbonic acid gas 22.—(2.) That the air is a mixture of 21 measures of oxygen, 78·93 of nitrogen, and 0·05 of carbonic acid gas. If x denote the sp. gr. of oxygen, y of nitrogen, and z that of carbonic acid gas (that of air = 1) then $0{\cdot}21\,x + 0{\cdot}7895\,y + 0{\cdot}0005\,z = 1$; moreover, $7x = 8y$; and $11x = 8z$. From this we find that the specific gravity of oxygen is 1·10926, that of nitrogen 0·9706, and that of carbonic acid gas 1·5252. From one of these three magnitudes, taken as a starting point, the specific gravities of the remaining substances have been calculated according to their atomic weights,—and from the same data it has likewise been determined whether they undergo 0, 1, 3, 6, 9, 12, 18, or 24-fold expansion in the gaseous state. The specific gravities of those substances which in the table have a note of interrogation put after them, have never been determined by direct experiment; in the hypothetical calculation of them it has been assumed, according to analogy, that the vapours of selenium and tellurium are 6-atomic, vapour of antimony 2-atomic, and the vapours of carbon, boron, fluorine, hydrofluoric acid, silicium, titanium, bismuth, and tin, are 1-atomic gases. The differences between the results of calculation and experiment are easily explained in the case of vapours, because the exact determination of their specific gravity is subject to great difficulties. The differences between the results of calculation and observation in the case of the permanent gases perhaps arise from the adoption of incorrect hypotheses in the calculation, *e. g.* the atomic weight of nitrogen may have been assumed too low. Since, however, the results of the most distinguished observers frequently differ more from one another than from the calculated specific gravity, a new and exact revision of the specific gravities seems to be required, to enable us to decide positively respecting the correctness or incorrectness of the assumed hypotheses.

One litre (or 1 cubic decimetre) of water at + 4° (its point of greatest density) weighs 1000 grammes. 1 litre of atmospheric air under the 45th parallel of latitude, at 0° C. and 0·76 met. atmospheric pressure, weighs, according to Biot & Arago, 1·2991 gramme (according to Dumas & Boussingault 1·2995). This gives for the weight at 4°,—since at this temperature (p. 224) the air is expanded $\frac{4}{273}$ of its bulk at 0° ($278 : 274 = 1{\cdot}2991 : x$), 1·28 gramme. To find the weight of a litre of any other gas at 0° and 0·76 met. bar. multiply the specific gravity of the gas by 1·2991 (the sp. gr. of air = 1). In this manner we may obtain with tolerable accuracy the relation by weight of water to the gas, since 1 litre of water weighs 1000 grammes; only it must be remembered that the weight of the gas is taken at 0°, and that of the water at + 4°. If we would find the relation between the specific gravities of the gas and water at the same temperature, viz. + 4°, we must assume that of water = 1000, and multiply the sp. gr. of the gas (that of air = 1) by 1·28.

According to the preceding, the specific gravity of air at 0°, and under a pressure of 0·76 metre, is to that of water at + 4° as 1·2991 : 1000; hence (since $1{\cdot}2991 : 1000 = 1 : 769{\cdot}7$) water is 770 times as heavy as air. If, then, the sp. gr. of air = 1, that of water = 770; and if the specific gravity (that of water = 1) of any liquid or solid body be multiplied by 770, the product will be its specific gravity, taking that of air = 1. On the contrary, to reduce the sp. gr. of a gas (air = 1) to what it will be, taking water = 1, we divide the former by 770. To find the expansion which a body undergoes in assuming the gaseous form, multiply its sp. gr. (water = 1) by 770 (the product will be its sp. gr. air = 1),

and divide this product by the sp. gr. (air = 1) which it has in the gaseous state; *e. g.*, in the case of water: 1·000 (sp. gr. of water) × 770 = 770; and 770 : 0·6239 (sp. gr. of vapour of water) = 1234·1;—for sulphur $\frac{2\cdot000\cdot770}{6\cdot6556} = 231\cdot4$; that is to say, 1 volume of water at 0° yields 1234·1 volumes of vapour of water at 0° and 0·76 met. pressure; and 1 volume of sulphur yields 231·4 volumes of sulphur vapour.

[Poggendorff's tables on the specific gravity of gases. (*Pogg.* 17, 259; 21, 629; 41, 449; 49, 416.)—Buff's method of determining the specific gravity of gases. (*Pogg.* 22, 242.) Dumas' Directions for determining the sp. gr. of gases. (*Ann. Chim. Phys.* 33, 341; also *Pogg.* 25, 236; also *Ann. Pharm.* 3, 59.) Mitscherlich's. (*Pogg.* 29, 193.)]

C. *Quantity of Heat in Gases.*

The quantity of combined heat in gases varies according to the nature of the ponderable body, and likewise according to the pressure to which the gas is subjected.

a. According to the Nature of the Ponderable Body.

The quantity of combined heat in the more permanent gases can only be approximately determined from the development of heat which takes place in the chemical combination of their ponderable elements with other substances to form non-gaseous compounds;—this development of heat is, however, partly due to the act of chemical combination. The quantity of heat set free in the absorption of acid gases and ammonia by water being but small, it would seem that these gases possess less heat of fluidity than vapour of water and some other vapours.

The quantity of heat in vapours is found by conducting a known weight of the vapour (produced by boiling the non-gaseous element in a retort) through a worm-tube, or into a receiver surrounded with a known quantity of water—or, in the case of vapour of water, directly into the water—and observing the increase of temperature produced in the water by the condensation of the vapour. This increase of temperature (expressed in degrees) multiplied by the volume of water in the receiver (the weight of the condensed vapour being assumed = 1) is equal to the heat of fluidity set free by the condensation of the gas, + the decrease of temperature which the condensed matter undergoes from its boiling point to the temperature exhibited by the water at the end of the experiment.—Persoz (*Chim. molec.* 250) heats the liquid to its boiling point, and then drops it with a pipette upon mercury, the temperature of which is about 50° above the boiling point of the liquid, till the mercury is nearly cooled down to that point,—and determines the quantity of heat which has become latent, by observing the temperature of the mercury before and after the experiment, the quantity of the mercury, and that of the liquid evaporated.

Table of the Latent Heat of Vapours.

Column A: Name of the substance.—B: Its specific gravity in the liquid or solid state.—C: Number of degrees centigrade above 0° which the vaporized body would exhibit at its boiling point, if none of the heat were rendered latent.—D: Deducting from this the heat required to raise the substance from 0° to its boiling point, the remainder is the quantity of latent

heat in the vapour at the boiling point.—E: Number of degrees by which the temperature of water at 0° would be raised by the quantity of heat which the same weight of vaporized matter at its boiling point would give up, if it were to lose its gaseous condition and be cooled down to 0°.—F: The same after deducting the quantity of heat required to heat the substance from 0° to its boiling point,—and found by multiplying the specific heat by the number of degrees at which the boiling point is fixed. This column F serves, therefore, for comparing the quantities of latent heat in different vaporized substances. If the numbers in columns E and F be divided by the specific heats of the respective substances, the quotients will give the numbers in columns C and D:—these numbers might be obtained directly by experiment if the vapours of the several substances were passed, not through water, but through the bodies from which they are respectively formed, *e. g.* vapour of alcohol through cold alcohol, &c. —G: name of the observer.

A	B	C	D	E	G	G
Water	1·0000	670°	570°	670°	570°	Rumford
——	—	650	550	650	550	Clem. Desormes
——	—	637	537	637	537	Ure
——	—	631	531	631	531	Despretz
——	—	624	524	624	524	Watt
Acetic acid	1·0007	—	—	—	485	Ure
Solution of ammonia ..	0·978	—	—	—	465	Ure
Hydrated nitric acid ..	1·495	—	—	—	295·5	Ure
Alcohol	0·793	410·7	331·9	255·5	207·7	Despretz
——	0·815	—	—	—	240	Gay-Lussac
——	0·825	—	—	—	245·5	Ure
Ether	0·715	210	174·5	109·3	90·8	Despretz
——	undetermined	—	—	—	168	Ure
Oil of turpentine, rect..	0·872	323	166·2	149·2	76·8	Despretz
——	undetermined	—	—	—	98·8	Ure
——	—	—	—	—	124	Gay-Lussac
Rock-oil	—	—	—	—	98·8	Ure
Sulphuret of carbon ...	—	—	—	—	80	Despretz

The quantities of heat required for vaporization appear to be to one another nearly in the inverse ratio of the densities of the vapours produced, and therefore also, in some measure, of the atomic weights of the corresponding substances: for on multiplying the latent heat of a vapour by its specific gravity, we obtain a set of numbers nearly equal to one another. If the latent heat belonging to the substance in its liquid state, which, however, is known only in the case of water, were added to the other portion of latent heat, a more exact coincidence would perhaps be obtained.—This law, however, does not yet agree with the results of experiment sufficiently well to entitle it to be considered as established. (*Comp.* Th. Saussure, *N. Gehl.* 4, 97; also *Gilb.* 29, 126; Ure, *Ph. Trans.* 1818, p. 385; also *Schw.* 28, 360; Despretz, *Ann. Chem. Phys.* 24, 323.)

¶. I subjoin the following table of the latent heats of vapours recently determined by the experiments of Favre and Silbermann

(*Comptes rendus*, 23, 524), and also of Andrews (*Qu. J. of Chem. Soc.* 1, 27). ¶.

Substance.	Lat. Heat of Vapour.	Obs.	Observer.	Lat. Heat of Vapour.	Obs.
Water	537·18	F S	Valerianic acid	103·52	F S
,,	535·90	A	Butyric acid	114·67	,,
,,	536·67	Rg	Acetic ether	105·80	,,
Bromine	45·60	A	,,	92·68	A
Protochloride of phosphorus	51·42	,,	Acetate of methyl	110·20	,,
			Formic ether	105·30	,,
Bisulphuret of carbon	86·67	,,	Formiate of methyl	117·10	,,
Bichloride of tin	3·053	,,	Iodic ether	46·87	,,
Alcohol	208·31	F S	Iodide of methyl	46·07	,,
,,	202·40	A	Oxalic ether	72·72	,,
Wood-spirit	263·86	F S	Butyrate of methyl	87·33	F S
,,	263·70	A	Ethal	58·44	,,
Fusel-oil	121·37	F S	Oil of turpentine	68·73	,,
Ether	91·11	,,	Terebene	67·21	,,
,,	90·45	A	Oil of lemons	70·02	,,
Amylic ether	69·40	F S	Hydrocarbons		
Acetic acid	101·91	,,	(*a*). $C^{12} H^{12}$ (B. P. 198°)	59·9	,,
Formic acid	120·72	,,	(*b*). $C^{15} H^{15}$ (B. P. 255°)	59·7	,,

b. According to the state in which one and the same vapour exists.

A given quantity of saturated vapour of any substance always contains the same total quantity of heat, whatever may be the pressure to which it is subjected, and whatever may be its elasticity and temperature: but of the heat thus contained in it, the quantity existing in the combined state increases as the pressure on the vapour diminishes, and consequently as its temperature falls,—while, on the contrary, the quantity of free or uncombined heat increases as the pressure is increased, and consequently as the vapour becomes hotter. (Sharpe, *Manch. Mem.* 1813; also *Ann. Phil.* 19, 302. Clement & Desormes, *Thénard, Traité de Chimie*, ed. 4, 1, 81. Pambour, *Institut*, Nr. 256.)

One pound of saturated aqueous vapour, at any temperature whatever, forms, with $5\frac{1}{2}$ lb. of water at 0°, $6\frac{1}{2}$ lb. of water at 100°, *i. e.* the vapour parts with 550° of heat, in order to become liquid water. Such is the case with aqueous vapour of 100° C. and a tension = 1 atmosphere, aqueous vapour of 152° C. and a tension = 4 atmospheres, and aqueous vapour of various other temperatures and tensions. (Clement & Desormes.) The vapour of water contained in the atmosphere at 0° contains 650° of combined heat. The temperature and elasticity of vapour of water increase as its volume diminishes. In a vessel, whose sides would permit neither ingress nor egress of heat, saturated vapour of water at 100° might, by enlargement of the space, be converted into cold vapour of low tension, and, by continual narrowing of the space, into very hot vapour of high tension, without any liquefaction taking place in the latter case (unless the space were to become too small to allow of the water existing in the gaseous state).

Estimating the latent heat of vapour of water at 100° C. as equal to 550° C. (990° F.), and the free heat = 100° C. (180° F.), we have

In Vapour of	Free Heat.	Latent Heat.		together.
0°	0°	650°	}	
50	50	600		
100	100	550		650°
150	150	500		
200	200	450		
250	250	400	}	&c. &c.

At 650° (1202° F.), no more of the heat could exist in the latent state. This temperature probably corresponds to a degree of external pressure at which the expansion of water into vapour becomes impossible, and beyond which all the heat remains accumulated in the water in the free state. Aqueous vapour below 0° would contain so many more degrees of latent heat as its temperature was under 0°; *e. g.* vapour of water at — 20° C. would contain 670° of latent heat.

¶. The law just stated is commonly known as Watt's law. According to Southern, on the contrary, the heat obtained by subtracting from the total heat the sensible heat indicated by the thermometer,—or that which is ordinarily called the latent heat of evaporation,—remains constant. The late elaborate researches of Regnault have shown that both these laws are incorrect.—Supposing the relation between the total quantity of heat and the temperature to be developed in a series of ascending powers of the temperatures, that is to say, of the form:

$$\lambda = A + Bt + Ct^2 + Dt^3 + \ldots$$

A, B, C.... being constants, the law of Watt would be expressed by $\lambda = A$. Regnault, on the contrary, finds that the law may be represented, within the limits of error of experiment, by $\lambda = A + Bt$,—and he obtains for A and B the values, A = 606·5, B = 0·305; so that the formula for calculating the total quantity of heat in steam at different temperatures becomes

$$\lambda = 606{\cdot}5 + 0{\cdot}305t.$$

Calculated by this formula, the preceding table becomes:

In Vapour at	Free Heat.	Latent Heat.	Sum.
0°	0°	606·5	606·5
50	50	571·7	621·7
100	100	537·0	637·0
150	150	502·2	652·2
200	200	467·5	667·5
250	250	430·25	682·7

[*Vid. Works of the Cavendish Society*, Vol. I. p. 294.] ¶.

D. *Liquefaction and Solidification of Gases.*

a. Liquefaction by external pressure and cooling.

Since, according to the preceding, every gas takes up a greater space than the liquid or solid matter out of which it is formed, it must, when the space which it occupies is continually diminished, ultimately lose its gaseous form, and be thereby deprived of its heat of fluidity.—If the sides of the vessel could be heated from without at exactly the same rate as the gas becomes hotter by compression; or, what comes to the same thing, if the compression could be produced in a vessel impervious to heat, liquefaction would not take place till a very considerable external pres-

sure was exerted, sufficient to diminish the space within limits no longer compatible with the existence of the gaseous form. Under ordinary circumstances, however, the sides of the vessel retain their former temperature, and consequently deprive the gas, whose temperature has been raised by compression, of its excess of heat; hence the liquefaction is effected by a much smaller pressure. The gaseous particles, cooled down by the sides of the vessel, and thus rendered less elastic, are pressed together by the rest; and, according to the contraction of the space, there remains either no gas uncondensed, or a quantity whose density and elasticity are in accordance with the existing temperature.

Bodies, when not prevented by external pressure, or perhaps in some cases by cohesion, appear to be capable of combining with heat, and forming gas, even at the lowest known temperatures: hence it is probably impossible to produce liquefaction by cooling alone. Accordingly, most liquefactions of gases are effected by the joint action of cooling and pressure.—The smaller the affinity of the ponderable substance for heat, or, in other words, the less the elasticity of its vapour at the same temperature, the smaller is the amount of external pressure and cooling required for destroying its gaseous condition. Thus vapour of water at 100° C., at which temperature its elasticity = 0·76 met. of mercury, is liquefied by a pressure somewhat greater than 0·76 metre; and at 0°, at which its tension = 0·00476 M. by a pressure somewhat greater than that.

Almost all the more permanent gases may be liquefied by pressure and cooling. Monge & Clouet liquefied sulphurous acid gas by cooling; Guyton Morveau liquefied ammonia; and Stromeyer arseniuretted hydrogen gas by similar means; but these experiments were disregarded, and their results partly attributed to the presence of small quantities of water, till Faraday (*Phil. Transact.* 1823, 160 and 189; also *Kastn. Archiv*, I, 97), partly in conjunction with Sir Humphry Davy, made known the mode of liquefying a considerable number of gases.

Faraday's usual mode of proceeding is as follows. He introduces the liquid required for generating the gas into the shorter and closed arm of a strong glass tube bent at an angle, places over it some folded platinum foil, fills the longer arm with the solid substance from which the gas is to be developed, seals the extremity, raises the shorter arm so that the liquid may run down amongst the solid matter and act upon it, and then, after leaving the tube to itself for a day or two, dips the shorter arm into a freezing mixture, and the longer arm into warm water: the liquefied gas then collects in the shorter arm. For carbonic acid, the materials are: oil of vitriol and carbonate of ammonia; for sulphuretted hydrogen: concentrated hydrochloric acid and protosulphuret of iron; for oxide of chlorine: oil of vitriol and chlorate of potash; for hydrochloric acid: oil of vitriol and sal-ammoniac. In cases in which the development of gas does not take place without the application of heat, Faraday puts the whole of the ingredients into the longer arm:—for sulphurous acid: mercury and oil of vitriol; for cyanogen: cyanide of mercury; for ammonia: ammonio-chloride of silver; for chlorine: hydrate of chlorine. Oxygen, hydrogen, nitrogen, nitric oxide, phosphuretted hydrogen, and fluoride of silicon, Faraday did not succeed in liquefying.—Niemann (*Br. Archiv*, 36, 175) places the ingredients in a glass tube sealed at one end, bends the tube at an acute angle about 8 or 10 inches from the sealed end, and after sealing the other end, cools the shorter arm, the length of which is only 2 or 3 inches, by means of snow or cold water, while the

longer arm is heated by the sun, or by water at temperatures between 30° and 38°. The tube must be very strong, and should not be struck hard or touched with sand; for as long as the development of gas is going on, the danger of bursting is continually on the increase. The bursting is attended with violent detonation, the tube being often split into innumerable fragments (Niemann). Hence it is necessary to wear gloves and a mask, with thick glasses before the eyes.

Bussy effected the liquefaction of chlorine, cyanogen, and ammoniacal gas at a pressure but little superior to the ordinary pressure of the atmosphere, by transmitting these gases through a tube closed with mercury, widened, and covered with cotton at one part,—while sulphurous acid was dropped upon the cotton, and a stream of air directed on it (p. 274).—These gases may likewise be condensed in a freezing mixture made with chloride of calcium.—A tube, in which solid carbonic acid has been sealed up, is found to contain nothing but gas when heated, while liquid carbonic acid makes its appearance in the cold. (Mitchell.)

¶ Faraday has lately succeeded, by the use of more powerful means, in liquefying all the known gases, with the exception of oxygen, hydrogen, nitrogen, nitric oxide, carbonic oxide, and coal-gas,—and solidifying a great number of them. (*Phil. Trans.* 1845, I. 170; abstr. *Phil. Mag. J.* 26, 253.) The method adopted was to subject the gases to the joint action of powerful mechanical pressure and extreme cold. The first object was attained by the successive action of two air-pumps, the first having a piston one inch in diameter, the second only half an inch. The first produced a pressure of about 20 atmospheres, the second increased it to upwards of 50. The tubes into which the gas thus condensed was made to pass were of green bottle glass, from $\frac{1}{6}$ to $\frac{1}{4}$ of an inch in external diameter, and had a curvature in one portion of their length adapted for immersion in a freezing mixture. The mixture employed consisted of solid carbonic acid and ether. The cold produced by it amounted to — 106° Fah. in the open air, and — 166° Fah. under the exhausted receiver of the air-pump.

Many gases, when subjected to this extreme degree of cold, were liquefied without the use of the condensing apparatus: this was the case with chlorine, cyanogen, ammonia, sulphuretted hydrogen, arseniuretted hydrogen, hydriodic acid, hydrobromic acid, carbonic acid, olefiant gas, nitrous oxide, and oxide of chlorine. Fluoride of silicon liquefied at a pressure of 9 atmospheres. The following were solidified when subjected to the action of the carbonic acid bath *in vacuo:* Hydriodic acid, hydrobromic acid, sulphurous acid, sulphuretted hydrogen, carbonic acid, oxide of chlorine, cyanogen, ammonia, and nitrous oxide. Faraday suggests the employment of solid nitrous oxide mixed with ether as a means of producing a lower temperature than any yet observed. The following gases did not solidify, even at the lowest temperature that could be obtained: Olefiant gas, fluoride of silicon, fluoride of boron, phosphuretted hydrogen, hydrochloric acid, and arseniuretted hydrogen.—The six gases mentioned at the commencement of the preceding paragraph showed no signs of liquefaction when cooled by the carbonic acid bath *in vacuo:* hydrogen and oxygen at 27 atmospheres, nitrogen and nitric oxide at 50, carbonic oxide at 40, and coal-gas at 32 atmospheres. ¶.

Every liquid may be regarded as a condensed gas, prevented by pressure from expanding itself in the gaseous form, but still retaining a por-

tion of its latent heat, which probably bears a simple relation to the whole quantity of latent heat existing in the gas. In an empty space of infinite extent, all solid bodies would, at all temperatures, be converted into gas, without previously melting: but when the empty space is of limited extent, it becomes filled with the gas that is formed; and this gas exerts a pressure on the remaining portion of the solid body, and renders it capable of fusion.

The decomposition of a gas by cooling or pressure is always attended with the formation of a *Cloud*. This cloud is a mixture of the uncondensed gas with the very finely divided liquid or solid particles which separate from the gas, and produce cloudiness by irregular refraction of light or by their opacity. When these particles are solid, the cloud is sometimes designated by the term *Fume*.

Daniell's *Sulphuric Ether Hygrometer* (*Qu. J. of Sc.* 1820; also *Gilb.* 65, 169 and 403) simplified by Döbereiner and Körner (*Gilb.* 70, 135 and 139) and improved by Adie (*N. Ed. J. of Sc.* 1, 60; abstr. *Schw.* 56, 459) depends for its action on the condensation of the aqueous vapour contained in the air by cooling.

Sublimation and *Distillation* depend on the conversion of a substance into vapour and the condensation of the vapour in another part of the apparatus by cooling. The object of both these operations is, for the most part, to separate an easily vaporized body from one which is less volatile. The former is converted into vapour, while the latter remains as the *residue* of the sublimation or distillation,—the so-called *Caput mortuum*, or in the case of its being liquid, the *Phlegma*, &c. of the older chemists. The operation is called *Sublimation*, when the vapour conducted into the colder part of the apparatus condenses into a solid substance, and *Distillation*, when the vapour is converted into a liquid. In both operations the body to be vaporized is enclosed in an *Alembic*, *Flask*, or *Retort*. On the top of the alembic or flask is fitted a *Head;* and this, during the distillation is often connected with a *Cooling* or *Condensing Tube* which passes into the *Receiver:* when a retort is used, the vapour passes through the neck into the receiver, which is kept cool, and there condenses. A tube widened in the middle is often placed between the receiver and the neck of the retort.—The vapours may also be conducted from the retort, the flask, or the head of the alembic through a glass or metal tube, and there they may be condensed either in the manner recommended by Liebig, viz., by Weigel's *Condensing Apparatus* (Taschenb. 1794, 129), in which the tube is surrounded with a metal cylinder through which cold water is continually flowing in a direction contrary to that of the vapour—or else by surrounding the tube with bibulous paper or linen kept moist by water constantly dropping on it.

Vapour, condensed into a solid body forms a *Sublimate;* that which condenses to a liquid, a *Distillate*. When the latter is subjected to a second distillation, to free it still further from less volatile bodies, the operation is called *Rectification:* by *Cohobation* is meant the distillation of the distilled product after it has been poured back either on what remains behind or on fresh material.

Since vaporization proceeds very rapidly in vacuo even at low temperatures, so likewise does distillation go on very quickly at low temperatures when the apparatus is exhausted of air, provided the receiver be kept colder than the retort. If, on the other hand, the apparatus be full of air, the substance must be heated to the boiling point; otherwise the distillation will be very slow. It will, however, be understood from what

was said on page 285, that the quantity of heat expended in the formation of vapour, is the same whether the vaporization takes place in vacuo or in a space filled with air, and at whatever temperature the vapour may be formed.

When a volatile liquid, like ether, is to be kept boiling for a considerable time in contact with another substance without allowing any of it to escape, a glass tube open at both ends is attached to the flask and kept cool with water by means of Weigel's condensing apparatus, or merely surrounded with moistened paper, so that the vapour which rises into the tube may be condensed and run back into the flask. Mohr's apparatus (*Ann. Pharm.* 18, 232); also Carriol and Berthemot's apparatus (*J. Pharm.* 18, 112).

b. Liquefaction or Solidification by the Affinity of Ponderable Bodies for the Ponderable Base of the Gas.

If any ponderable body, whether it be in the solid, liquid, or gaseous state, has a stronger affinity at the given temperature for the ponderable substance contained in a gas, than heat has for the same substance, and if this stronger affinity is able to exert itself (pp. 36...38), the two ponderable substances combine, and the latent heat of the gas (or of both gases, as the case may be) is rendered sensible, provided the new compound is not itself gaseous.

To this case belongs the condensation of oxygen gas by the combination of oxygen with hydrogen, boron, phosphorus, selenium, and metals; that of chlorine by combination with phosphorus, selenium, iodine, and metals; of acid gases by ammoniacal gas and many other salifiable bases; of all gases by water, alcohol, and other liquids; of aqueous vapour by acids, salifiable bases, salts and other bodies; of alcohol and ether vapours by water, oil of vitriol, fat oil, or camphor, &c.

When aqueous vapour at 100° is brought into contact with pulverized salts, citric acid, hydrate of potash, or sugar, these substances absorb part of the water and form a solution, the temperature of which is several degrees above 100°, and approaches very closely to the temperature at which the aqueous solutions of these substances boil (p. 269). Thus also alcohol vapour of 83·3° raises the temperature of chloride of calcium to 99°. (Faraday, *Ann. Chim. Phys.* 20, 320.) Aqueous solutions of acids and salts enclosed together with water in a vessel full of air at the ordinary temperature, absorb so much the more vapour of water, as their boiling points are higher: solutions of different substances whose boiling points are the same often absorb equal quantities of aqueous vapour. (Graham, *Edinb. J. of Sc.* 8, 326.)

Ronsdorff's Evaporating Receiver. (*Pogg.* 15, 604.) A basin filled with oil of vitriol is placed on a large glass plate, a number of cup-shaped glasses arranged in the basin, and on the top of these above the oil of vitriol are placed dishes containing the liquid to be evaporated. A glass bell jar is inverted over the whole, and kept close to the plate by means of grease. The evaporation goes on gradually at the ordinary pressure and temperature.

The hygrometer of De la Rive (*Bibl. univ.* 28, 285) is founded on the different degrees of temperature indicated by a thermometer exposed to the air after immersion in oil of vitriol—the rise of temperature being duced by the condensation of the aqueous vapour in the air, and vary- with the degree of humidity. It has however been shown by Gay-

Lussac (*Ann. Chim Phys.* 30, 89) that the density of the air likewise influences the rise of temperature.

Woulfe's Apparatus. To cause gases to combine with liquids, they are conducted by means of tubes twice bent at right angles, from the flask or retort in which they are generated, through a number of bottles, *Woulfe's Bottles*, which are furnished with two or three openings. The liquid contained in these bottles absorbs the gas as it enters in single bubbles. To prevent the liquid from passing back, the third opening is fitted, either with a straight tube open at both ends and dipping into the liquid, or else with a *Welter's Safety-tube, i. e.*, a tube twice bent, and having in the middle a bulb containing water.

Degrees of Incandescence, according to Pouillet.

525°: incipient redness;—700°: dull red; 800° commencing cherry-red; 900° brighter cherry-red; 1000° full cherry-red; 1100° dark yellowish red; 1200° bright ignition; 1300° white heat; 1400° strong white heat; 1500°...1600° dazzling white.

Melting Points.

	Cels.	Fah.		Cels.	Fah.
Carbonic acid	− 65°	− 85°	Phosphorus	+ 45°	+ 113°
Ether	− 44	− 47·2	Potassium	+ 58	+ 136·4
Mercury	− 40·5	− 40·9	Wax	+ 67	+ 152·6
Oil of vitriol	− 25	− 13	Sodium	+ 90	+ 194
Bromine	− 20	− 4	Iodine	+ 107	+ 224·6
Hydrocyanic acid .	− 15	+ 5	Sulphur	+ 109	+ 228·2
Water	0	+ 32	Camphor	+ 175	+ 347

	Guyton-Morveau (*Ann. Chim.* 90, 236).		Wedgwood & Dalton (*N. Syst.* 1,54).		Daniell.		Schwartz.	Rudberg.
	Cels.	Wedg.*	Cels.	Wedg.	Cels.	Dan.†	Cels.	Cels.
Bismuth	247	—	247	—	239	66	260	264
Tin	267	—	246	—	227	63	220	228
Lead.....	312	—	322	—	321	87	340	325
Zinc.....	374	3	371	—	342	94	500	
Antimony	513	7	432	—			620	
Brass	—	—	—	—	1021	267		
							Pouillet.	Prinsep.
Silver	1034	22	—	28	1223	319	1000	999
Copper.....	1207	27	—	27	1398	364		
Gold.....	1381	32	—	32	1421	370	1200	
Cobalt	—	—	—	130				
White Cast Iron..	—	—	—	—	—	—	1100	
Grey ,, ..	4783	130	—	—	1915	497	1210	
Steel.....	—	—	—	—			1350	
Manganese	5825	160	—	160				
Bar iron	6346	175					1550	
Nickel, Platinum, Iridium, Rhodium, Quartz..	above	175						

* Degrees c
† Degrees

Boiling Points.

Sulphurous acid.....	− 10°	Water	+ 100
Hydrochloric ether.....	+ 12	Oil of turpentine	157
Nitric ether.....	21	Iodine	180
Hydrocyanic acid	26·5	Camphor	284
Sulphuric ether	35·66	Oil of vitriol.....	288
Sulphuret of carbon	46·6	Phosphorus	250
Bromine.....	47	Sulphur	293
Alcohol	78·41	Mercury	356
Rock-oil.....	65·5	Selenium (nearly)	700

II. Disengagement and Absorption of Heat.

1. *By Chemical changes in Ponderable Substances.*

A. *By alteration of the state of Aggregation.*

It has already been shown that the passage of a solid body to the liquid state, and that of a liquid or solid to the gaseous state, is always accompanied by absorption of heat; and that when these substances are brought back to their former condition, the heat is again set free.

B. *By the combination of Ponderable Bodies one with the other, and decomposition of the resulting Compounds.*

The combination of ponderable substances, with or without the destruction of existing compounds, is always accompanied by disengagement or absorption of heat.

The most striking instances of the *Development of Heat* are those which accompany the production of light, as noticed on page 181, those namely which take place in the combination of oxygen and chlorine with metals and other combustible bodies,—of bromine, iodine, sulphur, and phosphorus with several metals; likewise in the combination of strong acids with strong salifiable bases, and in that of strong acids and strong bases with water,—in all cases, that is to say, in which combination is brought about by strong affinity, and in which the combining bodies are decidedly opposite in chemical nature.

To determine the quantity of heat set free in combustion, the process is made to go on in a space surrounded with water or ice, and the quantity of ice melted, or the rise of temperature in a given quantity of water, observed.

In the following table, Column A contains the name of the combustible substance;—B its symbol or formula;—C the formula of the compound produced during the combustion;—D shows how many parts of water are heated 1° by the combustion of 1 part of the combustible body, or the number of degrees by which the temperature of 1 part of water would be raised;—E the name of the observer;—F shows how many parts of water are heated 1°, when 1 part of oxygen combines with the combustible substance.—If we would find how many units of heat are developed by the burning of 1 atom of the combustible body, we must multiply the number in column D by the atomic weight of the substance: similarly by multiplying the numbers in column F by 8, we obtain the quantity of heat which 1 atom of oxygen develops in combining with the different substances.

Cr denotes Crawford;—Da: Dalton;—Dg: Dulong;—Dz: Despretz;—

Hs: Hess;—Lv: Lavoisier;—Rf: Rumford. When two results by the same observer are given, the first is denoted by [1], the second by [2].

¶ I have likewise added the more recent determinations by Grassi (Gr), Favre & Selbermann (FS), and Andrews (A).

A	B	C	D	E	F
Hydrogen	H	H O	20624	Dz^2	2578
			21375	Lv	2672
			23640	Dz^1	2955
			24000	Da	3000
			34743	Dg	4343
			34792	Hs	4349
			36000	Cr	4500
			34666	Gr	4333
			34662	F S	4333
			33808	A	4226
Carbon	C	CO^2	3000	Da	1125
			5175	Cr	1941
			5325	Rf	1997
			7012	C D	2629
			7167	Dg	2688
			7237	Lv	2714
			7815	Dz^1	2931
			7912	Dz^2	2967
			7714	Gr	2893
			7900	A	2962
Carbonic oxide	C O	CO^2	1875	Da	3031
			2634	Dg	4609
			1854	Gr	3244
			2431	A	4254
Phosphorus	P	PO^5	4500	Da	3532
			7500	Lv	5696
			5747	A	4509
Sulphur.....	S	SO^2	1500	Da	1500
			2571	Hs	2571
			2601	Dg	2601
			2307	A	2307
Antimony	Sb	SbO^4	961	Dg	5875
Zinc	Zn	Zn O	1314	,,	5290
			1301	A	5366
Tin.....	Sn	SnO^2	1233	Dg	4545
			1144	A	4230
Protoxide of tin.....	Sn O	SnO^2	534	Dg	4473
			521	A	4349
Iron	Fe	Fe^3O^4	1702	Dg	4340
			2088	Dz	5325
			1576	A	4134
Cobalt	Co	Co O	1080	Dg	3995
Nickel	Ni	Ni O	1006	,,	3723
Copper	Cu	Cu O	632	,,	2512
			602	A	2394
Suboxide of copper	Cu^2O	2Cu O	241	Dg	2185
			256	A	2288
Cyanogen	C^2N	$2CO^2$, N	5195	Dg	4241
Marsh gas	CH^2	CO^2, 2H O	6375	Da	1594
			13185	Dg	3296
			11098	Gr	2774
			13158	F S	3289
			13108	A	3277

A	B	C	D	E	F
Olefiant gas	C H	CO^2, H O	6600	Da	1925
			12030	Dg	3296
			8436	Gr	2461
			11900	F S	3471
			11942	A	3483
Alcohol	$C^4H^6O^2$	$4CO^2$, 6H O	4350	Da	2084
			6750	Rf	3234
			6909	Dg	3311
			6566	Gr	3146
			7183	F S	3442
			6850	A	3282
Ether	C^4H^5O	$4CO^2$, 5H O	4650	Da	1792
			8025	Rf	2093
			9431	Dg	3634
			9027	F S	3480
Wood spirit	$C^2H^4O^2$	$2CO^2$, 4H O	5839	Gr	3893
			5304	F S	3536
Fusel-oil	$C^{10}H^{12}O^2$	$10CO^2$, 12H O	8959	,,	3285
Amylic ether	$C^{10}H^{11}O$	$10CO^2$, 11H O	10188	,,	3353
Acetone	C^3H^3O	$3CO^2$, 3H O	7320	,,	3317
Rock oil	C H	CO^2, H O	7335	Rf	2139
Oil of turpentine	C^5H^4	$5CO^2$, 4H O	4500	Da	1339
			10496	Gr	3187
			10874	F S	3301
Oil of lemons	$C^{10}H^8$	$10CO^2$, 8H O	10663	,,	3237
Terebene	,,	,,	10959	,,	3327
Camphor	$C^{10}H^8O$	$10CO^2$, 8H O	5250	Da	1847
Olive oil			6675	Cr	
			7800	Da	
			9045	Rf	
			9862	Dg	
			11100	Lv	
Rape-oil			9300	Rf	
Tallow			7800	Da	
			8370	Rf	
Wax			7273	Cr	
			7800	Da	
			9472	Rf	
			9975	Lv	
Caoutchouc			2105	Da	
Oak-wood			2970	Rf	
Elm-wood			3480	,,	
Coal		4575	..5625	,,	
Turf		1200	..1725	,,	

The quantities of heat furnished by other kinds of wood are intermediate between those yielded by oak and elm. (Rumford.) [For more on this matter, *vid. Woody Fibre.*] One part of oxygen produces with phosphorus, zinc, or tin 5325 units of heat, the same quantity therefore as with iron, and $1\frac{1}{2}$ times as much as with carbon. The quantity of heat evolved by charcoal during its combustion is the same under whatever pressure the oxygen gas may exist. Since the volume of carbonic acid gas produced is equal to that of the oxygen consumed, it follows that oxygen gas and carbonic acid gas must contain the same absolute quantity of heat. In the combustion of metals, on the other hand, in which oxygen suffers condensation, the quantity of heat must be greater as the pressure to which the gas is subjected is less. (*Ann. Chim. Phys.* 37, 180 and 182; also *Pogg*, 12, 519 and 520.) Dulong's determination of the

quantity of heat developed in the combustion of carbonic oxide is doubtless too high; if it were correct, we should be obliged to admit, what is highly improbable, that carbon would develope much less heat in combining with the first atom of oxygen than with the second.

According to the approximate results of Davy (*Schw.* 20, 143), on the other hand, a given quantity of oxygen, which, in combining with carbon evolves a quantity of heat = 1, gives out 1·12 in combining with sulphuretted hydrogen gas, 1·6 with olefiant gas, and 4·3 with hydrogen. At all events, the law enunciated by Welter (*Ann. Chim. Phys.* 19, 425; 27, 223), viz. that any given quantity of oxygen evolves the same quantity of heat, with whatever combustible body it may combine—is at present very doubtful. It would rather appear from a comparison of the numbers in column F, that oxygen developes a greater quantity of heat, the stronger its affinity for the combustible substance.

¶ The following table gives the quantities of heat evolved in the combination of different substances with chlorine. (Andrews, *Phil. Mag. J.* 32, 426.) The results are expressed as in the preceding table, the numbers in column A referring to the combination of a unit of weight of the several substances in the left hand column, and those in column B to the combination of a unit of weight of chlorine.

	A	B
Potassium	2655	2943
Tin	1079	897
Antimony	707	860
Arsenic	994	704
Mercury		822
Phosphorus	3422 ?	607
Zinc	1529	1427
Copper	961	859
Iron	1745	921

By comparing the numbers in column A with the corresponding numbers in column D of the former table (pp. 292, 293), it will be seen that the heat evolved in the combination of a substance with chlorine is in some cases greater and in others less than in the combination of the same substance with oxygen. ¶.

Development of Heat in the Combination of Compound Bodies (according to Hess).—The bodies are here compared according to their atomic weights. When it is said that one atom of sulphuric acid, in combining with excess* of water, produces 20202 units of heat, it is to be understood that 40 parts of sulphuric acid (= 1 atom) develope in this combination a quantity of heat sufficient to raise the temperature of 20202 parts of water by 1°, or that of 1 part of water by 20202°.

If one atom of anhydrous sulphuric acid combines first with 1 At. water, then with 1 more atom, and so on, the quantities of heat produced are as follows:

			Units of Heat.	Therefore with excess of Water,
SO^3	gives with	HO:	12432 = 8 . 1554	20202 = 13 . 1554
HO, SO	,,	HO:	3108 = 2 . 1554	7770 = 5 . 1554
$2HO, SO^3$	,,	HO:	1554 = 1 . 1554	4662 = 3 . 1554
$3HO, SO^3$	,,	3HO:	1554 = 1 . 1554	3108 = 2 . 1554
$6HO, SO^3$	,,	∞ HO:	1554 = 1 . 1554	1554 = 1 . 1554
			20202 = 13 . 1554	

* *i. e.*, with such a quantity of water that any further addition would produce no more developement of heat.

If these 1554 units of heat be called an equivalent of heat, it will be seen from this that sulphuric acid, in combining with water, evolves 13 such equivalents, 8 in uniting with the first atom of water, 2 with the second, &c.

1 atom of hydrochloric acid (= 36·4 parts) in the form of aqueous hydrochloric acid of 1·125 sp. gr. (in which it is already combined with 12 atoms of water) evolves 3233 units of heat when mixed with more water.

One atom of nitric acid (54 parts) developes the following quantities of heat, according to the quantity of water which it previously holds in combination.

	Units of Heat.	Therefore with excess of Water,
H O, NO^5 with H O:	1554 = 1 . 1554	7770 = 5 . 1554
2H O, NO^5 ,, H O:	1554 = 1 . 1554	6216 = 4 . 1554
3H O, NO^5 ,, 2H O:	1554 = 1 . 1554	4662 = 3 . 1554
5H O, NO^5 ,, H O:	777 = ½ . 1554	3108 = 2 . 1554
6H O, NO^5 ,, 2H O:	777 = ½ . 1554	2331 = 1½ . 1554
8H O, NO^5 ,, ∞H O:	1554 = 1 . 1554	1554 = 1 . 1554
	7770 = 5 . 1554	

H O, NO^5 developes therefore, on the whole, as much heat in combining with water as H O, SO^3 does, and the heat-equivalent is the same for both; differences are however met with in individual instances.

One atom of well fused hydrate of potash (47·2 potash + 9 water) gives with excess of water 12920 units of heat.—1 atom of well burnt lime (28·5 parts) yields 6520.

With excess of dilute ammonia, potash, or soda, or with lime slaked with excess of water, 1 atom of sulphuric acid gives the following units of heat according to the quantity of water previously combined with it:

	Ammonia.	Potash.	Soda.	Lime.
H O, SO^3:	23840	23886	24348	25640
2H O, SO^3:	20756	21080		22584
3H O, SO^3:	19220	19320		
6H O, SO^3:	17846	17720	17896	19568

The greater therefore the quantity of heat which the sulphuric acid has already evolved in combining with water, the less does it give out when saturated with ammonia. If to the 23840 units of heat which H O, SO^3 gives with ammonia, there be added the 12432 which SO^3 gives with water, the result is 36272 for the sum of the units of heat which would be developed in the combination of 1 atom of anhydrous sulphuric acid with aqueous solution of ammonia. If from the heat which H O, SO^3 developes in combining with aqueous ammonia there be deducted that which it would develope in combining with water alone, the remainder (23840 — 7770) will be the heat which is set free on the further addition of ammonia, viz. 16070. Similarly for the other alkalis. According to this, 1 atom of sulphuric acid evolves the same quantity of heat, whether it combines with ammonia, potash, or soda: the more powerful development of heat in the case of lime is perhaps due to the combination of water with the sulphate of lime produced. One atom of dry sulphate of lime immersed in water developes 1680 units of heat; this deducted from 25640 leaves 23960, as much therefore as for the other alkalis.

One atom of aqueous hydrochloric acid of 1·125 sp. gr. (containing

12 At. water, 12 H O, H Cl, = 144·4 parts) developes with dilute ammonia 14764, with dilute potash 14476, with dilute soda 14720, with burnt lime and water 24110, and with lime previously slaked with water (since, according to the above, 6520 units of heat are thereby evolved) 17588 units of heat. 14764 (heat with ammonia and water) — 3233 (heat with water alone) = 11531 (heat developed by the further addition of ammonia).

One atom of nitric acid containing 8 atoms of water (8H O, N O^5 = 126 parts) yields with dilute ammonia 16172, with dilute potash 16378, with dilute soda 16402, and with slaked lime 18048 units of heat. 16172 (heat with ammonia and water) — 1554 (heat with water alone) = 14618 (heat on the further addition of ammonia).

Whilst ammonia, potash, and soda, yield equal quantities of heat by combining with sulphuric acid, and similarly with hydrochloric and nitric acid, lime gives a larger quantity,—a fact which Hess explains by supposing that the lime-salts, even in solution, contain water of crystallization. If this however be admitted, the same should take place with sulphate of soda. The difference probably consists in this, that the first three alkalis are capable of combining with excess of water, in which combination they have already evolved heat, whereas slaked lime has taken up only one atom of water.

One atom of chloride of calcium (55·9 parts) gives with excess of water 9456 units of heat; since however 1 atom of crystallized hydrated chloride of calcium (Ca Cl, 6HO = 109·9 parts) when dissolved in water, causes 1346 units of heat to disappear, the actual development of heat amounts to 9456 + 1346 = 10802.—Thus far Hess.

¶ Andrews (*Phil. Trans.* 1844, I., 21; abstr. *Phil. Mag. J.* 24, 457) has shown that when one base displaces another from any of its neutral combinations, the heat evolved or abstracted is always the same, whatever the acid may be, provided the bases are the same.—The base employed for displacing the others was the hydrate of potash in a state of dilute solution of known strength. The changes of temperature, referred to 1000 parts of water, were found to be, with salts of:

Lime	— 0·36°	Oxide of zinc	+ 1·74°
Baryta	0·0	Protoxide of mercury	+ 1·86
Strontia	0·0	——— lead	+ 2·82
Soda	+ 0 08	——— copper	+ 3·00
Ammonia	+ 0·74	Oxide of silver	+ 3 93
Manganese	+ 1·07	Peroxide of iron	+ 4·09
Protoxide of iron	+ 1·60		

The differences in the results of experiments with different acids were not greater than usually occur in chemical reactions, on account of the uncertainty that exists with regard to the values of chemical equivalents.

Andrews has likewise shown that if 3 metals A, B, C, are so related that A is capable of displacing B and C from their combinations, and also B capable of displacing C,—then, the heat evolved in the substitution of A for C is equal to that developed in the substitution of A for B, together with that which would be evolved in the substitution of B for C: and the law may be extended to any number of metals similarly related.

[For Graham's researches on the development of heat in the combination of acids and bases, &c., vid. *Phil. Mag. J.* 22, 351, and 24, 401.] ¶.

The heat developed in these combinations, some of which must be regarded as combustions, may proceed from four distinct sources.

(*a*) From the specific heat of the compound being less than the mean of the specific heats of the combining substances (Crawford). In most cases, however, the atoms of simple substances retain their original specific heat when they enter into combination (pp. 248....251). In other cases, on the contrary, combination is attended with an actual increase of specific heat, so that the result would be a production of cold, if heat were not developed from some other cause.

Thus, 1lb. of hydrogen gas of 3·293 specific heat combines, under the most violent evolution of heat, with 8lb. of oxygen of specific heat 0·236, producing 9lb. of water of specific heat 1·000,—whereas calculation gives $\left(\frac{3{\cdot}293 + 8 \,.\, 0{\cdot}236}{9}\right) = 0{\cdot}576$ as the mean of the two specific heats. If then water had a specific heat = 0·576, the quantity of sensible heat in hydrogen and oxygen gases together would be exactly sufficient to bring the water formed to the same temperature as that of the gases themselves: but since the actual specific heat of water is 1·000, the quantity of sensible heat in the gases is not sufficient for this purpose; and if heat were not developed from some other cause during the combination of oxygen and hydrogen, the water produced would be much colder than the two gases before combination.

b. The heat developed may arise from separated heat of fluidity, if, during the combination, gaseous or liquid substances pass to the liquid or solid state. This however will not account satisfactorily for the more intense evolutions of heat in combustions and other combinations: for the latent heat of gases and liquids is small in comparison with such developments of heat. Moreover, in many instances the combination is not attended with condensation; *e. g.* in the combustion of charcoal and sulphur in oxygen gas, and of hydrogen in chlorine gas; or again, gaseous products are formed from solid bodies, great heat being at the same time evolved, as in the explosion of nitre with charcoal, &c.

c. The heat evolved may be a kind of heat different from heat of fluidity, producing no particular state of aggregation, but existing in a state of more intimate chemical combination with the ponderable matter, and set free when one ponderable substance combines with another.

d. The heat is formed at the moment of combination by the union of the positive electricity of the one body with the negative electricity of the other.

Either the cause adduced under *c*, or that in *d*, or both together, must be admitted, in order to explain the development of heat which accompanies the combination of ponderable bodies. (See the observations on the *Theory of Combustion* under the head of *Oxygen*.)

Cold is produced (1) Principally in some of those chemical combinations in which solid bodies pass to the liquid state,—combinations which are brought about by feeble affinities, the quantity of heat developed being probably far from sufficient to render the dissolving body liquid, so that more heat must be absorbed and rendered latent to supply heat of fluidity: *e. g.* in the solution of various salts in water and dilute acids, and more especially on mixing these salts, as well as certain acids, crystallized potash, or alcohol, with ice or snow,—though the same substances, when mixed with water, evolve heat. (*Freezing Mixtures*.)

Such of these substances as contain water of crystallization must not be deprived of it; otherwise, when mixed with water, they will produce

heat instead of cold.—The more finely the substances are pulverized, the more quickly they are mixed, the larger their quantity, and the smaller the conducting power of the containing vessels, the greater will be the degree of cold produced.—To produce the greatest possible degree of cold, the substances of which the freezing mixture is to be made are cooled, before mixing, in another freezing mixture.—With respect to this matter, it must be observed that a solution of common salt in water is completely resolved at − 20° into ice and crystallized salts; therefore, common salt and snow cooled to this point no longer act on one another; whereas with chloride of calcium and snow the corresponding point is as low as − 60°, and with sulphuric acid and snow much lower; so that this mixture, when the ingredients have been properly cooled, is capable of producing the most intense degree of cold. (Murray.)

One part of water, in dissolving 1 part of nitrate of ammonia, produces a lowering of temperature from + 10° to − 15·5°; with $\frac{5}{16}$ sal-ammoniac and $\frac{5}{16}$ nitre, from + 10° to − 12°; with 1 part of nitrate of ammonia and 1 part of carbonate of soda, from + 10° to − 13·8°; with 0·3 sal-ammoniac, 0·1 nitre, and 0·6 chloride of calcium, from + 25° to − 6°; with $\frac{3}{16}$ sal-ammoniac, $\frac{5}{16}$ nitre, and $\frac{8}{16}$ Glauber's salt, from + 10° to − 15·5°; 1 part of water likewise produces a considerable degree of cold with $\frac{1}{2}$ sal-ammoniac, $\frac{1}{2}$ nitre, and $\frac{3}{4}$ Glauber's salt; or with $\frac{9}{40}$ sal-ammoniac, $\frac{10}{40}$ nitre, and $\frac{16}{40}$ Glauber's salt. (Walker.)

By dissolving 1 part of a salt in 4 parts of water, the following reductions of temperature are obtained: sal-ammoniac 15·19°; nitrate of ammonia 14·1°; sulphate of potash 2·9°; chloride of potassium 11·81°; nitre 10·6°; Glauber's salt 8·1°; common salt 2·1°; nitrate of soda 9·46°; chloride of barium 4·5°; nitrate of baryta 2·1°; sulphate of magnesia 4·5°; sulphate of zinc 3·1°; nitrate of lead 1·9°; sulphate of copper 2·27°. —If 1 part of a salt be dissolved in 4 parts of a saturated solution of another salt, the following degrees of cold are produced: sal-ammoniac in solution of common salt 8·4°; in solution of nitre 12·6°;—nitre in solution of sal-ammoniac 9·75°; in solution of common salt 9·4°; of nitrate of soda 7·06°; of nitrate of baryta 9·75°; of nitrate of lead 9·5°;—Glauber's salt in solution of common salt 4·75°;—common salt in solution of sulphate of copper 4·1°; nitrate of soda in solution of sal-ammoniac 9·1°; of nitre 9·2°; of common salt 7·81°; of chloride of barium 2·75°; of nitrate of lead 8°;—nitrate of baryta in solution of nitre 0·75°;—sulphate of zinc in solution of sulphate of potash 1·75°;—sulphate of copper in solution of common salt 4·9°.—The following salts, on the contrary, produce rise of temperature: common salt in solution of sal-ammoniac 4·56°; in solution of Glauber's salt 1·75°; of nitre 0·75°; of nitrate of soda 3·8°;—chloride of barium in solution of nitrate of soda 0·64°. (Karsten, *Schriften d. Berl. Akad.* 1841.)

Three parts of crystallized neutral carbonate of soda dissolved in 10 parts of water produce a lowering of temperature amounting to 8·9°, whilst 3 parts of the same salt in the anhydrous state dissolved in 10 parts of water cause a rise of temperature of 12·2°.—3 parts of crystallized Glauber's salt with 10 parts of water produce a fall of 6·7°; on the contrary, 3 parts of dry Glauber's salt with 10 parts of water cause a rise of 2·2°.—3 parts of crystallized sulphate of magnesia with 10 parts of water produce a fall of 3·1°; and 3 parts of crystallized protosulphate of iron with 10 parts of water also produce a fall of temperature amounting to 3·1°. (Thomson, *Records of Gen. Sc.* 1836, July; also *Bibl. univ.* 5, 182; also *J. pr. Chem.* 13, 176.)

One part of a mixture of 50 parts of oil of vitriol and 55 water, mixed with $1\frac{1}{2}$ parts of Glauber's salt, cools from + 10° to − 8°.—One part of dilute hydrochloric acid with $1\frac{3}{4}$ Glauber's salt, from + 10° to − 17·8°. —1 part of dilute nitric acid gives the following reductions of temperature: with 1 sal-ammoniac, $\frac{1}{2}$ nitre, $1\frac{1}{2}$ Glauber's salt, from + 10° to − 12°;—with $1\frac{1}{4}$ nitrate of ammonia and $2\frac{1}{4}$ phosphate of soda, from + 10° to − 6°; with $2\frac{1}{4}$ phosphate of soda, from + 10° to − 11°;—and with $1\frac{1}{2}$ Glauber's salt, from + 10° to − 16°. (Walker.)

Cooled mixtures of oil of vitriol and water in different proportions give with Glauber's salt, according to Bischof and Wöllner (*Schw.* 52, 371), the following reductions of temperature.

Oil of vitriol.	Water.	Glaub. salt.	
500	208	885	22·50°
500	250	937	26·25
500	300	990	26·25
500	333	1040	27·50
500	416	1150	26·75
500	500	1000	26·25
500	500	1250	24·37
500	635	1400	19·06
500	750	1560	18·41

Six parts of oil of vitriol produce heat with 6 parts of snow, neither heat nor cold with 8 parts, and intense cold with a larger quantity of snow. (*Stöchiom.* 1, 2, 87.)

Cheap freezing mixtures for producing ice in summer, with description of the apparatus: 4 parts of a cooled mixture of 50 oil of vitriol and 55 water, with 5 parts of Glauber's salt, or 9 parts of hydrochloric acid of 15° B. with 14 parts of Glauber's salt. (Decourdemanche, *J. Pharm.* 11, 584; also *N. Tr.* 14, 2, 249.)—12 parts of a mixture of 3 oil of vitriol and 2 water with 17·5 parts of Glauber's salt. (Malapert, *J. Pharm.* 21, 221; also *Ann. Pharm.* 18, 348.)—3 parts of a mixture of 7 oil of vitriol and 5 water with 4 parts of Glauber's salt. (Boutigny, *J. Chim. Méd.* 10, 460.)

One part of snow or pounded ice produces the following degrees of cold: with $\frac{1}{3}$ dilute sulphuric acid (4 oil of vitriol and 1 water) from 0° to − 32·5°;—with 1 dilute sulphuric acid from − 7° to − 51°. (I have also obtained a considerable degree of cold by mixing the crystallized compound of 49 oil of vitriol and 9 water with snow);—with $\frac{1}{2}$ dilute nitric acid, from − 23° to − 49°;—with 1 dilute nitric acid, from − 17·8° to 43°;—with $1\frac{1}{3}$ crystallized potash, from 0° to − 28°;—with $\frac{1}{2}$ common salt, from 17·8° to − 20·5°;—with 1 common salt, from 0° to − 17·8°;—with $\frac{5}{1\,2}$ common salt and $\frac{5}{1\,2}$ nitrate of ammonia, from − 27·8° to − 31·7°;—with $\frac{1}{2}$ chloride of calcium, from − 9° to 42·5°;—with $1\frac{1}{4}$ chloride of calcium, from 0° to − 49°;—with $1\frac{1}{2}$ chloride of calcium, from 0° to − 27·8°, and from − 7° to − 47°;—with 2 chloride of calcium, from − 17·8° to 54·4°, and with 3 chloride of calcium, from − 40° to − 58°; and, according to Tralles (*Gilb.* 38, 365), with absolute alcohol, from 0° to − 36·9°, with highly rectified spirit from, 0° to − 30°.

Orioli (*Nuov. Collez. di Op. Scient.* 1823, 104; also *Fersasac Bull. des Sc. Math. Phys. et Chim.* 1825, 117) obtained, on mixing solid amalgam of lead with solid amalgam of bismuth—the two substances at the same time becoming liquid—a reduction of temperature amounting to 22°. According to Döbereiner (*Schw.* 42, 182; also *Kastn. Arch.* 3, 90), 204 parts of lead-amalgam (consisting of 103 lead and 101 mercury) mixed

with 172 bismuth-amalgam (71 bismuth + 101 mercury) cool from +20° to −1°; if to this mixture there be also added 202 parts of mercury, the temperature falls to −8°. When a finely-divided mixture of 59 tin, 103·5 lead, and 182 bismuth is dissolved in 808 parts of mercury, the temperature falls from + 17·5° to −10°.

2. The mixture of liquids is in some few instances attended with reduction of temperature, condensation taking place at the same time. This effect is perhaps due to the greater specific heat of the mixture.—Thus, on mixing 44 parts of a concentrated aqueous solution of nitrate of ammonia, sp. gr. = 1·302, with 34 parts of water at 16° C. the temperature falls 5°, and the mixture has a specific gravity of 1·159, the mean sp. gr. being 1·151. Similar effects are produced on mixing several other saline solutions with water; but the reduction of temperature is not so great.

With the same quantity of water, a saturated solution of chloride of potassium gives a reduction of temperature of 0·75°; that of common salt, of 0·56°. A saturated solution of nitre gives with a saturated solution of nitrate of soda a rise of 0·06°; but an equal weight of water added to this mixture produces a fall of 1·25°. Saturated solutions of the following salts produce, when mixed in equal quantities, the following degrees of cold: sal-ammoniac and nitre 0·62°; sulphate of potash and nitre 0·44°; chloride of barium and sulphate of zinc (accompanied by precipitation) 2°; sal-ammoniac with excess of sulphate of copper 1·6°,—whereas when the sal-ammoniac is in excess, a rise of 1·6° takes place. (Karsten, (*Schriften d. Berl. Akad.* 1841.)

2. *Development and Absorption of Heat from Mechanical Causes.*

A. *Development of Heat accompanying Adhesion-Phenomena.*

When any liquid substance penetrates finely divided bodies by capillary attraction, no chemical combination taking place between the two, a rise of temperature takes place, amounting in the case of inorganic solid bodies to between $\frac{1}{5}$ and $\frac{1}{2}$°, but with organic bodies—probably because they are more porous and therefore present a larger surface—to between 1° and 10°. (Pouillet.)

Pouillet's experiments were made with water, alcohol, acetic ether, and oils; the solid inorganic bodies into which he caused these liquids to penetrate were the filings of different metals, the powders of sulphur, glass, porcelain clay, various earths, and heavy metallic oxides; and the organic substances, charcoal, wood-shavings, cotton, paper, roots, seeds, flour, hair, wool, animal skins, &c. The development of heat from this cause has been confirmed by Regnault. (*Ann. Chim. Phys.* 76, 133.)

B. *Development of Heat, produced by Mechanical Alteration of Density.*

Every mechanical compression or condensation of a body, even if it does not produce a change in the state of aggregation, is attended with evolution of heat; every expansion of the body, on the contrary, though unattended with actual change of aggregation, gives rise to absorption of heat. The development of heat by compression is probably due chiefly to diminution of specific heat in consequence of increase of density; the absorption of heat by expansion to increased capacity for heat,—and the more so, since the development of heat is greater in proportion to the degree of condensation.

Air when suddenly compressed evolves a considerable degree of heat, sufficient to ignite German tinder (*Fire-syringe*). According to Thénard, (*Ann. Chim. Phys.* 44, 181; also *Pogg.* 19, 442) paper, oiled paper, and wood may also be ignited by sudden compression in oxygen gas, and oiled paper in chlorine gas; also fulminating silver may be made to detonate in hydrogen, nitrogen, or carbonic acid gas.—The great reduction of temperature which takes place in air under the receiver of the air-pump on sudden expansion may be strikingly shown by means of the delicate thermoscope of Breguet.—Liquids, which are but slightly compressible, evolve but little heat when subjected to pressure. Under a pressure of 40 atmospheres, water exhibits scarcely any rise of temperature, alcohol only 1°, and ether 4° or 5°. (Colladon & Sturm, *Pogg.* 12, 161.)—Metals become hot and even red-hot by hammering, their density at the same time increasing. In the stamping of coin, the development of heat produced by the first blow is greater than that produced by the second or third: the increase of density is likewise greatest at the first blow. Copper coins become more heated than silver, and silver than gold; the specific gravity also increases most in the copper and least in the gold. (Berthollet, Pictet, Biot.) In the boring of cannon with iron borers great heat is evolved, whether the operation be performed in ordinary air, rarefied air, or water. (Rumford.) When an iron rod is broken by hanging weights to it, it lengthens considerably before breaking and becomes very hot. (Barlow, *Ann. Phil.* 10, 311.) An alloy of 1 part of iron and 2 of antimony emits sparks when filed. (Becquerel.) On a revolving grindstone 7½ feet in diameter an iron nail becomes white-hot in ¼ minute, brass red-hot in ½ minute; a glass tube becomes red-hot, melts and flies off. (Heinrich.) Agate rubbed on the same grindstone gives off sparks which travel with the grindstone for a little distance—the agate also becomes brightly red-hot. The glowing fragments which fly off from glass rubbed on the grindstone set fire to gunpowder (according to Wedgewood). Two pieces of wood take fire when rubbed hard together. When rough glass is rubbed on smooth, the former becomes more strongly heated than the latter; similarly, rough cork on smooth; when white satin is rubbed on black, the former is most strongly heated; on rubbing together smooth glass and cork, the rise of temperature in the two is as 34 : 5; with ground glass and cork as 40 : 7; silver and cork as 50 : 12; caoutchouc and cork as 29 : 11. (Becquerel, *Ann. Chim. Phys.* 70, 239.)

III. Influence of Heat on the Chemical Combinations and Decompositions of Ponderable Bodies.

The influence of heat on the chemical combinations of ponderable bodies in which it acts partly as the principle of fluidity, partly in a manner unknown, has been considered (pp. 36 and 37). Of decompositions of ponderable substances produced by heat, an account has been given pp. 119...122, and 132...166.

¶ The most remarkable instance of decomposition by heat is the resolution of water into its constituent gases by the agency of incandescent platinum, lately discovered by Mr. Grove. (*Phil. Mag. J.* 30, 58; 31, 96.) A platinum wire is sealed into the closed extremity of a kind of tube-retort, having its neck narrowed close above the wire. The tube is filled with pure water, and the current of a voltaic battery made

Chapter III.

ELECTRICITY.

Th. Andrews. Thermo-Electricity. *Phil. Mag. J.* 10, 433; also *Pogg.* 41, 164.

——— Conducting power of Flame. *Phil. Mag. J.* 9, 176; also *Pogg.* 43, 310.

Armstrong. Electricity by Expansion of Air and Aqueous Vapour. *Phil. Mag. J.* 18, 133, 328 and 500; 19, 25; 20, 5; 21, 1; 22, 194; *Ann. Chim. Phys.* 75, 328; *Pogg.* 52, 328.

Becquerel. Electricity by Pressure. *Ann. Chim. Phys.* 22, 5; *Thermo-electricity*, 23, 135 (also *Schw.* 39, 448); *Chemical Electricity*, 23, 152; 23, 244 (also *Schw.* 40, 385); 23, 259 (also *Schw.* 40, 405); 24, 203; *Electricity by Capillarity*, 24, 237 (also *Schw.* 40, 408); *Chemical Electricity*, 24, 348; 25, 405 (also *Schw.* 43, 71; also *Pogg.* 2, 169); 26, 176 (also *Schw.* 44, 153; also *Pogg.* 2, 180); 27, 5 (also *Pogg.* 2, 191); 27, 14 (also *Pogg.* 2, 201); 28, 19, and 27 (also *N. Tr.* 11, 1, 236); *Thermo-electricity*, 31, 371 (also *Pogg.* 9, 345); *Chemical Electricity* 34, 153 (also *Pogg.* 11, 457); 35, 113. Electricity by Cleavage of Crystals, 36, 265 (also *Pogg.* 12, 147); Electricity by Wire in Flame, 36, 328 (also *Pogg.* 11, 437); Crystal-electricity, 37, 5, and 355 (also *Pogg.* 13, 628); Friction-electricity of Metals, 38, 113 (also *Pogg.* 13, 619); Compounds produced by Electricity, 41, 5 (abstr. *Pogg.* 16, 306); Thermo-electricity, 41, 353 (also *Pogg.* 17, 535); Combinations and Decompositions by Galvanic Action, 42, 226 (also *Pogg.* 18, 143; also *Schw.* 58, 439); 43, 131 (also *Pogg.* 18, 147); 43, 380; Thermo-electricity, Friction-electricity, and Chemical Electricity, 46, 265, and 337; Galvanic Decompositions, 48, 337; Electricity developed in the Cementation of Iron by Charcoal, 49, 131; Platinum with Gold, Peroxide of Manganese, Black Lead, 60, 164; Galvanic Formation of Carbonate of Lime, 60, 173; Galvanic Apparatus with Nitric Acid and Potash, *Bibl. univ.* 60, 215; also *Pogg.* 37, 429.—Also *Ann. Chim. Phys.* 66, 84; also *Pogg.* 44, 437.—Electric Current, which decomposes, but does not produce Heat. *Bibl. univ.* 59, 218; also *Pogg.* 37, 433.

Becquerel (E). Conducting Power of Solids and Liquids. *N. Ann. Chim. Phys.* 20, 53.

Van Beek. Metals with Sea-water. *Pogg.* 12, 274; again, *Ann. Chim. Phys.* 64, 225.

Beetz. Certain Phenomena of Voltaic Decomposition. *Pogg.* 61, 209.—Rusting of Iron, and its Connection with the Passive State, 92, 234.—Voltaic Polarization of Iron, 63, 283.—Passivity of Iron, 67, 186.

Berzelius & Hisinger. Galvanic Decomposition of Salts. *Gilb.* 27, 270.

Berzelius. Galvanic Action on Coloured Papers. *Gilb.* 27, 316.—Theory of the Electric Pile. *N. Gehl.* 3, 177.

Binks. Laws of Galvanism. *Phil. Mag. J.* 11, 62; 12, 54, 135, 171, and 276.

G. Bischof. Voltaic Pile. *Kastn. Archiv.* 4, 13.—Electric Series of Metals. *Schw.* 52, 230.

R. Böttger. Thermo-electricity. *Pogg.* 50, 41.—Nobili's Rings. *J. pr. Chem.* 8, 476.—Electricity produced by Tin with Nitrate of Copper. *Ann. Pharm.* 29, 77.—Galvanic Tinning, Gilding, Platinizing, and Zinking. *Ann. Pharm.* 34, 84; 35, 221, and 350; 39, 171.—Electrotype. *Ann. Pharm.* 35, 216; 39, 180.—Production of pure Iron in the coherent State by Galvanic Electricity. *Pogg.* 67, 117.

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A. Connel. Galvanic Decompositions. *N. Edinb. Phil. J.* 19, 163; *Phil. Transact. of Edinb.* 13; also *J. pr. Chim.* 5, 167; *Phil. Mag. J.* 18, 353.

Callan. New Voltaic Battery. *Phil. Mag. J.* 31, 81.

Cumming. Thermo-electricity. *Ann. Phil.* 21, 427; 22, 177 and 321; also *Schw.* 40, 312 and 317.

Daniell. Voltaic Combinations. *Phil. Transact.* 1836, 1, 107; abstr. *Pogg.* 42, 262.—Galvanic Decompositions. *Phil. Transact.* 1838 and 9; abstr. *Ann. Pharm.* 36, 32.—Electrolysis of Salts. *Phil. Mag. J.* 22, 461.—Electrolysis of Secondary Compounds. *Phil. Mag. J.* 24, 463.

Daniell & Miller. Electrolysis of Secondary Compounds. *Phil. Mag. J.* 25, 175.

J. Davy. Iron with Tin; Galvanism without Chemical Action. *N. Edinb. Phil. J.* 17, 42 and 46.

H. Davy. Galvanic Decompositions. *N. Gehl.* 5, 1; also *Gilb.* 28, 1 and 162.—Electricity in vacuo. *Phil. Transact.* 1822, 64; also *Gilb.* 72, 357.—Protection of Copper by Iron. *Phil. Transact.* 1825, 328; also *Schw.* 56, 434; *Ann. Chim. Phys.* 33, 319.—Chemical and Electric Actions. *Ann. Chim. Phys.* 33, 276; also *N. Tr.* 15, 1, 84.

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Hare. Calorimotor and Deflagrator. *Ann. Phil.* 14, 176; also *Schw.* 26, 313.—*Ann. Phil.* 17, 329; 2, 328; 4, 119.

Hauy. Electricity by Pressure and Friction. *Ann. Chim. Phys.* 5, 95; 8, 383; also *Schw.* 20, 383; 25, 135.—*J. Phys.* 89, 455.

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Henrici. Galvanism. *Pogg.* 47, 431; 48, 372; 52, 387; 53, 277; 58, 61 and 232.—Influence of Temperature on the Conducting Power of Liquids for Galvanic Currents. *Pogg.* 66, 174.—Theory and Application of Electricity. *Phil. Mag. J.* 27, 164.

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—Galvanometer, 48, 26.—Galvanic Circuits, 50, 510.—Grove's Battery, 53, 336.—Galvanic Reduction of Brass, 62, 230—Galvanic and Electro-magnetic Experiments, 68, 161, 181, 188 and 207.

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The term *Electricity* is applied, according to the dualistic theory of Dufay and Symmer, to two imponderable fluids, very similar in their properties, but diametrically opposed in their mutual relations;—or, according to the theory of Franklin, to a single imponderable fluid, the relative excess or deficiency of which is supposed to produce the phenomena of *Positive* and *Negative Electricity**.

Properties.

1. The two Electricities are imponderable.
2. They diffuse themselves uniformly and with the greatest rapidity through those spaces which they are able to penetrate.

* The dualistic theory is not only better adapted to the chemical view of electrical phenomena, but likewise affords a much more satisfactory explanation of the distribution of electricity. For how is it possible, on the Franklinian hypothesis, to form a clear conception of the manner in which a body deficient in electricity, and placed in the neighbourhood of another containing electricity in excess, exhibits a still greater deficiency on the side nearest to the latter, and an excess on the opposite side (*a*)? The approximation of a hot and a cold body does not appear to be accompanied by any phenomena, resembling the distribution of electricity. The experiment of Moll (p. 315) is also favourable to the dualistic theory.

¶ (*a*). The Franklinian theory is perfectly competent to the explanation of this and every other phenomenon of statical electricity. The fundamental principles of that theory may be stated as follows: I. The particles of the electric fluid repel each other and attract those of ponderable matter. II. The particles of ponderable matter repel each other, and attract those of the electric fluid. III. In the ordinary state of a body, the quantity of electric fluid contained in it is such, that the attractive force exerted by the ponderable matter of the body on a particle of electric fluid situated without, is exactly balanced by the repulsive force exerted by the electric fluid of the body on the same particle. IV. A body containing *more* than this *natural* quantity of electric fluid is said to be *positively* electrified, and a body containing *less* than its natural quantity is said to be *negatively* electrified.—Now suppose a body A, negatively electrified, to be brought into the neighbourhood of a body B, positively electrified. The excess of electric fluid in B repels the fluid still remaining in A towards the end farthest from B, thus leaving the nearer end of A more negative than before,—and at the same time the redundant ponderable matter in A attracts the electric fluid in B towards itself, thus rendering the nearer end of B, more positive, and the farther end less positive than before. A similar explanation will apply to every case of statical induction. Indeed it is only necessary to state *the two theories* in precise terms, in order to see that any phenomenon of statical electricity which is explicable by the one, must of necessity be explicable by the other also,—the redundant matter of the one theory producing, in fact, the same effects as the negative electric fluid of the other. The difference between the two theories is that the one supposes a single and the other a double transfer of electric fluid to take place, in all cases of charge and discharge: but this makes no difference in the ultimate distribution of the positive and negative charge, which is all that we are concerned with in phenomena like that just noticed. The author's remarks in the preceding note seem to be based upon the notion that a body negatively electrified is supposed, according to the Franklinian theory, to be absolutely deprived of electric fluid. Such however is not the case, any more than we suppose a cold body to be absolutely deprived of heat. As to the experiment of Moll alluded to in the same place, I will only observe that the perforation of a card or a piece of tinfoil by the electric discharge, by no means obliges us to suppose that the electric fluid or fluids are bodily carried through the perforations.—In making these remarks, I would not be understood to advocate the theory of a single electric fluid in preference to the other,—or indeed the existence of an electric fluid at all: my object is merely to point out the perfect similarity of explanation, afforded by the two theories, of all the phenomena of ordinary electricity. [For a full development of the theory of Franklin (or rather of Æpinus) I must refer to *Robison's Mechanical Philosophy*, *Brewster's Edition*, vol. IV.; also to the admirable treatise of Dr. Roget in the *Library of Useful Knowledge*, *Natural Philosophy*, vol. II. The latter work, pp. 60....64, contains a concise and able comparison of the two theories.] ¶

To the class of *good Conductors of Electricity* belong the metals, certain metallic sulphurets, both natural and artificial, scale oxide of iron, peroxide of manganese, peroxide of lead, graphite, and charcoal.

Electricity travels along a copper wire faster than light moves in the celestial spaces, and with the same velocity from the positive to the negative end as in the contrary direction. If a copper wire of the length of $\frac{1}{3}$ an English mile be cut through in the middle, and its extreme ends brought near to the inner and outer coatings of Leyden jar, the spark will appear at the two coatings at the same instant, but somewhat later in the middle. (Wheatstone, *Ph. Tr.* 1835, ii. 583; also *Pogg.* 34, 464.) The conducting power of metals deminishes as their temperature rises. (De la Rive.) Solid mercury conducts electricity better than the same metal in the liquid state. (De la Rive.)

Conducting Power of Metals.

	Lenz.			H. Davy.	Becquerel.	Christie.
	at 0°	at 10°	at 200°			
Silver	136·25	94·45	68·72	109	73·6	100
Copper	100·00	73·00	54·82	100	100	66
Gold	79·79	65·20	54·49	73	93·6	73
Tin	30·84	20·44	14·78	—	15·5	17
Brass	29·33	24·78	21·45			
Iron	17·74	10·87	7·00	14·5	15·8	15
Lead	14·62	9·61	6·76	6·9	8·3	8
Platinum	14·16	10·93	9·02	18	16·4	16
Zinc	—	—	—	—	28·5	37
Mercury	—	—	—	—	3·4	
Potassium	—	—	—	—	1·3	

If the conducting power of copper at 19° = 100, that of antimony = 8·87, of mercury 4·66, and of bismuth 2·58. (Lenz.)—According to Pouillet, the conducting powers of platinum, copper, and palladium are as 2·5 : 16 : 30.

If it be assumed that metallic wires of equal thickness will be more strongly heated by the passage of an electric current in proportion as their conducting power is less, the following conducting powers may be deduced from the degrees of heat actually produced: Copper, silver, and alloys of 1 part copper with $\frac{1}{3}$, 1 or 3 parts silver, 100;—gold, 66·6—zinc, brass, and alloy of 1 part tin with 8 parts copper, 33·3;—an alloy of 1 part gold and 1 silver, 30;—an alloy of 1 part gold with 1 silver or $\frac{1}{3}$ copper, 24;—an alloy of 1 part tin and 1 zinc, 22·2;—platinum and iron, 20;—an alloy of 3 parts tin and 1 zinc, 18·8;—tin, 16·6;—an alloy of 3 parts tin and 1 lead, 13·3;—an alloy of 1 part tin and 1 lead, 11·1;—an alloy of 1 part tin and 3 lead, 9·5;—lead, 8·3. (Harris, *Phil. Transact.* 1827; abstr. *Pogg.* 12, 279.)

Ignited copper wire conducts better than the same wire unignited; and soft steel better than that which has been hardened. (Peltier.)—The conducting power of a wire of any given metal varies directly as its transverse section and inversely as the square of its length. (Christie.)

Among ores, copper-nickel is the best conductor; then follow purple copper, copper pyrites, and copper-glance, all three of which conduct well; then,—regularly diminishing in power,—iron pyrites, arsenical pyrites, galena, arsenical cobalt, peroxide of manganese, Tennantite and Fahlerz. (R. W. Fox, *N. Edinb. J. of Sc.* 4, 266.)

The feeble thermo-electric current of a single pair of bismuth and

antimony is very well conducted by sulphuret of bismuth, galena, scale oxide of iron, protosulphuret of iron, iron pyrites, arsenical pyrites, copper-glance, artificial disulphuret of copper, and purple copper;—moderately well by peroxide of manganese and peroxide of lead;—not sensibly, when the surface of contact is small, by blende, tinstone, protosulphuret of tin, magnetic iron ore, specular iron, wolfram, suboxide of copper solidified after fusion, red oxide of mercury, and cinnabar. It is remarkable that $Mn O^2$ and $Pb O^2$ should conduct electricity so well, seeing that Mn O and Pb O do not transmit the current even of a powerful battery. (Faraday.)

Imperfect Conductors or Semi-conductors.

a. Solids. Chalk and other minerals, earthenware, sulphuret of molybdenum, and tin pyrites.

Marekanite conducts electricity well under 19°; less freely at a higher temperature, and not at all at 37·5°: moisture is not the cause of the difference. Similar properties are exhibited by common obsidian, iolite, and many lavas. (P. Erman, *Pogg.* 25, 657.)

Sulphuret of silver, both natural and artificial, and likewise red silver, conduct the electricity of a battery of 20 pairs, feebly when cold, but more and more readily as they become hotter, and at a certain temperature almost as well as a metal: on cooling, their conducting power again decreases. Fluoride of lead solidified and cooled after fusion, does not conduct the current; but when heated to redness it conducts very well, and fuses by the heat which the current excites. (Faraday.)

b. Liquids. Water when pure is a very bad conductor of electricity, but acquires considerable conducting power by dissolving a variety of substances, even such as do not conduct of themselves, *e. g.*, bromine, iodine, chlorine, and sulphurous acid; it likewise converts solid insulators (such as silk) into semi-conductors by moistening them. (De la Rive.) The conducting power (and decomposibility) of water are most highly augmented by phosphoric, sulphuric, nitric, and oxalic acid, potash and soda, carbonate and nitrate of potash, carbonate of soda, many other salts, metallic chlorides and iodides; then follows carbonate of ammonia; then tartaric and citric acid. The following have no influence on the conducting power of water: boracic and acetic acid, ammonia, cyanide of mercury, sugar, and gum. (Faraday.)

Under a pressure of 30 atmospheres, the conducting power of water does not diminish; that of aqueous nitric acid diminishes a little. (Colladon & Sturm.)

Oil of vitriol conducts less easily than dilute sulphuric acid; the maximum of conducting power is possessed by a mixture containing 30 per cent. of anhydrous sulphuric acid; an acid containing 20 per cent., and likewise one of 43 per cent, conduct less freely; and one containing 64 per cent, much less. (De la Rive.)—The conducting power of watery liquids is increased by heat, probably because their decomposition is thereby facilitated. (De la Rive.)

The following substances, which are non-conductors in the solid state, become conductors when fused: Iodine (Inglis), ice, hydrate of potash, oxide of antimony, oxide of bismuth, protoxide of lead; the iodides of potassium, zinc and lead; protiodide of tin, protiodide of mercury; the chlorides of potassium, sodium, barium, strontium, magnesium, manganese, lead, zinc, and silver; terchloride of antimony, protochloride of tin, dichloride of copper; fluoride of potassium, fluoride of lead (see the

sulpho-cyanide of potassium; carbonate, silicate, manganate, chromate and bichromate, borate, phosphate, and nitrate of soda; nitrate and nitrate of strontia; acid phosphate of lime (*Phosphor-glas*), phosphate, sulphate, and nitrate of lead; phosphate sulphate of mercury and nitrate of silver.

of liquids by the electric current as connected with power will be considered further on.

by heat or exhaustion is a conductor. The more com- above the mercurial column is freed from air and vapour the latter is the light produced by electricity passing through The most perfect vacuum obtainable by the air-pump conduct nearly so well as metals: when the metallic conductors a considerable distance from one another, the electricity through. (Harris, *Pogg.* 41, 99.)

vacuum does not conduct the current of a voltaic (Masson, *Institut. Nr.* 249.)

of a single pair of zinc and copper plates in water acidu- sulphuric acid passes slowly—as may be seen by the decompo- iodide of potassium introduced into the circuit—through the charcoal urged by the bellows, that of hydrogen gas, coal gas, and other, even when the metallic conductors are placed 1/4 inch passes through the charcoal flame more easily, and through that less easily, than through the flame of alcohol. But even with 20 pairs, the current is very feeble, the tension of the pole diminution, because the electricity is generated faster than it Flame conducts positive electricity better than negative Hence the conduction is more complete when the negative coiled into a coil, and its surface thereby made larger than that of wire. When the negative wire is placed in contact with the and the positive wire in the flame, the current passes more when the arrangement is made the contrary way. Moreover, flame in which the two polar wires are placed, there be intro- wire in contact with the earth, the tension of the positive because the positive electricity is carried off, while that pole increases. In the heated air above the flame of an conduction takes place from one wire to another; negative wire be connected with the brass cylinder of the lamp positive wire wound into a spiral form and introduced into the the flame, conduction will take place,—but not when the in the contrary way, on account of the difficult con- negative electricity. (Andrews.)

Insulators (Faraday's *Dielectric Bodies*).

boron, phosphorus, sulphur, selenium, iodine,—. zinc-blende, bismuth-glance, cupreous bismuth, sulphuret of lead, black oxide of iron, green cyanide of mercury, cyanide of silver (gently oak-wood (Walcker),—the substances enume- becoming conductors when fused (Faraday),—oil, wool and hair.

are non-conductors both in the solid and in

the fused state: phosphorus, sulphur, boracic acid, green glass, iodide of sulphur, biniodide of tin, realgar, orpiment, glacial acetic acid, a mixture of tallow and oleic acid, camphor, naphthaline, artificial camphor, tallow, cocoa-fat, spermaceti, common resin, sandarac, shellac, sugar, and caffein. (Faraday.)

b. Liquids. Besides those above enumerated: bromine, chlorine, and sulphurous acid. (De la Rive.)

Terchloride of arsenic and its hydrate, and bichloride of tin. (Faraday.) Olive-oil conducts the electricity of a Zamboni's pile less quickly than other fat oils: solid tallow does not conduct so well as oily fat; and solid animal fat more slowly than the same when liquid. (Rousseau, *Ann. Chim. Phys.* 25, 373.)

c. Elastic fluids. Air and all other gases under the ordinary atmospheric pressure and at ordinary temperatures, are perfect insulators. They conduct so much the more quickly as their density is diminished.

A conducting body surrounded by non-conductors is said to be *Insulated*.

¶ Gutta Percha has lately been shown by Faraday to be one of the best among non-conducting bodies, its insulating power being fully equal to that of shellac. It may be used in the form of either sheet, rod, or filament. When formed into cylinders about half an inch in diameter, it forms excellent insulating pillars; and in the form of fine threads, it is exceedingly convenient for insulating light bodies, such as feathers, pith-balls, &c. A sheet of it is easily converted into an electrophorus, or it may be coated and used as a Leyden jar. When rubbed, it shows negative electricity.—All specimens of gutta percha are not equally good as insulators. The cut surface of a piece which insulates well has a resinous lustre and a compact character, which is very distinctive; whilst that which conducts has not the same degree of lustre, appears less translucent, and has more the aspect of a turbid solution solidified. By heating it in a current of hot air, as over the chimney of a low gas-flame,—and then stretching, doubling, and kneading it for a time between the fingers, as if with the intention of dissipating the moisture within, its insulating power may be made equal to that of the best specimens. (*Phil. Mag. J.* 32, 165.) ¶.

For methods of determining the conducting power of bodies for electricity of small tension, *vid.* Wollaston (*Phil. Trans.* 1823, 20); Rousseau (*Ann. Chim. Phys.* 25, 373).

The difference between conductors and insulators is one of degree only. Electricity of high tension like that developed by the electrical machine—and in a less degree, that of a voltaic battery of 150 pairs of plates—is conducted even by ice, and still better by iodide of potassium. The communication of one kind of electricity, either to conductors or non-conductors, first produces a polarization of their particles, a peculiar electric distribution,—so that the particle situated next to the one at which the electricity enters, takes up the opposite kind of electricity, the next particle the electricity opposite to that, and so on throughout the whole mass. This produces a discharge of electricity between the neighbouring particles: the sooner this takes place, and the smaller the electrical tension required to produce it, the better does the body conduct; the more slowly the discharge takes place and the higher the tension required to produce it, the better does the body insulate. Conductors cannot

remain permanently polarized; insulators, on the other hand, retain their polarized condition firmly. (Faraday.)

3. The two electricities exist in bodies in the state either of rest or of motion.

a. At rest. Peltier's *Statical Electricity.*

α. Either positive or negative electricity may be accumulated in insulated *conductors* in various quantities. The greater this quantity in proportion to the surface of the conductor (it is immaterial whether the conductor be hollow or solid) the greater is the *electrical Intensity* or *Tension* of the conductor, and the stronger the effort which the electricity makes to leave the conductor and unite with the opposite electricity in its neighbourhood; and this greater tension probably gives rise to more rapid motion when the electricity is conducted away.

β. In an *Insulator* the two kinds of electricity are always present at the same time, because the accumulation of one electricity at a particular point of such a body always causes by polarisation the appearance of the other electricity at the opposite point; and the tension of the two electricities is higher, the greater their quantity in proportion to the surface;—they also adhere to the insulator very strongly, so that they can only be gradually removed by conductors, unless the latter touch the whole surface of the insulator.

b. In Motion. Peltier's *Dynamical Electricity.* The two electricities issuing from two sources or two conductors charged with them meet in a conductor and combine together, and thus produce an *Electrical Current.*

CHEMICAL RELATIONS.

I. Relations of the two Electricities to one another.

The two electricities have a very great affinity for each other, and exert a powerful tendency to combine together. From their combination results *Latent* or *Quiescent Electricity,* which, according to the electrochemical theory, is nothing else than light and heat.

By various causes, the latent electricity in bodies is resolved into positive and negative electricity, which are set free at various points.

1. Combination of the two Electricities with each other.

When a body in which positive electricity is accumulated is brought near another charged with negative electricity, the two electricities combine together; and if they are present in equal quantities, both bodies appear perfectly neutral after the combination has taken place. The combination is attended with the development of light, heat, and magnetic phenomena. Insulators which oppose the combination are often violently torn asunder.

The tendency of the two electricities to unite shows itself, when the two bodies in which they exist are moveable, in an approximation of the bodies themselves:—Bodies oppositely electrified attract each other.

If the two bodies are separated by a thin film of a non-conductor, the

two electricities break through it—provided they have sufficient tension—and a spark is produced accompanied by a noise. (*Electric Shock.*) The duration of an electric spark is, according to Wheatstone, only $\frac{1}{115200}$ second. If the non-conductor be solid, like glass, it is pierced; the same effect takes place even with semi-conductors and good conductors—as with a card or tinfoil—when they are surrounded with air and placed in a thin film between the two oppositely electrified conductors. When a card is pierced in this way, the edges of the hole are often raised in the direction of both conductors, positive as well as negative. Tinfoil, according to Moll (*J. Phys.* 90, 396), often exhibits two holes with their edges turned in opposite directions, as if the positive electricity had gone through the one and the negative through the other.

The light of the spark is variously coloured, partly according to the density of the elastic medium, partly according to its peculiar nature. (H. Davy, *Ann. Chim. Phys.* 20, 168: Grotthuss, *Schw.* 14, 163; Faraday.)

When the combination of the two electricities takes place through a conductor brought in contact with both the electrified bodies, and the quantity of the combining electricities is considerable, the conductor becomes heated to the most vivid incandescence, and fuses. Platinum and iron wire fuse in the circuit of a powerful voltaic battery; if the wire be immersed in water, the water boils. A given quantity of common electricity heats a wire to the same degree, whatever may be its intensity. (Harris.)—Currents from different voltaic batteries which produce equal deflections of the magnetic needle, raise the temperature of the conducting wire in the same degree: if a wire 0·1 metre in length produces a deviation of 20°, and becomes heated 10°, a wire several metres long will also have its temperature raised 10°, when, by a proportionate increase in the power of the battery, its deviating power has been made equal to 20°. With the same wire, an augmentation in the power of the battery raises the temperature in a higher proportion than it increases the deflecting power: when the deflecting power is doubled, the degree of heating is trebled. With wires of different thicknesses, the heating power increases more rapidly than the transverse section diminishes; when the latter is reduced one-half, the former is increased three-fold. (Peltier.) If the connecting wire of the voltaic battery consists of three pieces of platinum and three pieces of silver soldered together alternately, the platinum alone becomes red-hot. If a platinum and a silver wire are connected together, the platinum becomes red-hot before the silver: so likewise platinum with zinc or gold. When platinum is joined with tin or lead, the latter metals fuse at the junction before the platinum becomes heated to redness; but even in this case the greatest rise of temperature takes place in the platinum. When platinum and iron are united, the platinum becomes first incandescent, then the iron more strongly than the platinum. When iron is united with gold or zinc, the iron becomes incandescent. Zinc is more strongly heated than silver, copper more strongly than gold. The more slowly metals conduct, the more intensely do they become heated; and according to these experiments, they succeed one another in the following order, beginning with the best conductors: Silver, zinc, gold, copper, iron, platinum. At high temperatures, iron seems to conduct less easily than platinum; for after the action has continued a certain time, the iron becomes the more incandescent of the two. (Children, *Phil. Tr.* 1815, 363; also *Schw.* 16, 359.) If a concentrated solution of chloride of calcium be connected with the positive pole of a strong voltaic

battery by a thick wire, and with the negative pole by a thin wire of platinum, the latter becomes incandescent, fuses, and falls into the solution in drops which follow one another very quickly; but if the thin wire conveys the positive electricity, it ignites but does not fuse. (Hare.) —A metal becomes the more strongly heated, the more slowly it conducts and the less capacity it has for heat. (Riess, *Pogg.* 44, 78.)

If a zinc wire be soldered to an iron or copper wire, the point of junction becomes more strongly heated when the zinc is connected with the negative than when it is connected with the positive pole. If the compound wire consists of copper and bismuth, the junction becomes heated when the copper is connected with the positive, but cooled when that metal is in connection with the negative pole. The opposite relation is exhibited when copper is united with antimony, the cooling taking place when the copper touches the positive pole. Antimony and bismuth give the strongest variations of temperature, exhibiting a rise of temperature at the junction when the positive electricity proceeds from the antimony, and a fall in the contrary case.

[Many metals, especially antimony, appear to conduct positive better than negative electricity; others, particularly bismuth, seem to be more capable of conducting negative electricity than positive. When antimony is connected with the positive, and bismuth with the negative pole, the former conducts positive and the latter negative electricity to the junction, which becomes heated from the combination of the two electricities; but when the antimony is connected with the negative pole, the heat of the junction is resolved into positive electricity, which passes on to the negative pole through the antimony which conducts it most freely,—and negative electricity which passes on, through the bismuth which gives it the readiest passage, to the positive pole. The combination of the two electricities and the consequent development of heat take place where the antimony touches the negative, and the bismuth the positive pole; but the junction is cooled by the decomposition of a portion of its heat*.]

The cooling of the junction amounts to 3° R; water placed in a hole made at that point becomes frozen in five minutes, if the rod has been previously cooled down to 0°. When the experiment is continued for a longer time, the temperature of the junction again rises, because the bismuth becomes gradually heated (much sooner than the antimony,) and communicates its temperature to the junction. (Lenz.)

If the copper wires connecting the poles of a Daniell's battery of 160 pairs be gradually separated to the distance of $\frac{1}{3}$ or $\frac{1}{4}$ inch, the electrical current will pass from one to the other in the form of a luminous arch (probably carrying fine particles of the conductor along with it). The positive wire alone becomes incandescent. Similar phenomena are exhibited by brass, iron, and platinum wires. (Gassiot, *Phil. Mag. J.* 13, 436; also *Pogg.* 46, 330.) [This seems to show that the negative electricity of the luminous arch is conducted more readily than the positive electricity, and that consequently the two electricities combine together in the wire.]

Charcoal placed between the poles of the deflagrator emits as much light as 1600 candles. (Hare.)

If the direction of the conducting wire is from North to South and a

* All remarks enclosed within three-cornered brackets contain explanations according to the author's theory given in *Pogg.* 44, 1, which, whether established or not, may serve as a guide to conduct us through the chaotic region of the theory of electricity, however much it may leave unexplained.

magnetic needle is placed in its neighbourhood and parallel to it, the needle changes its direction, even when the electricities which are combining in the wire have but a very feeble tension, provided only their quantity be sufficiently great. When the positive electricity enters at the north end of the wire and the negative electricity at its south end, and the magnetic needle is placed above the wire, the north pole of the needle turns to the west; if the needle is below the wire, its north pole turns to the east. If the needle is placed on the same level with the wire and on its eastern side, the north pole moves upwards; but the same pole acquires a downward motion, when the needle is placed on the western side of the conductor. We may imagine that the two electricities move through the wire towards one another in spiral lines, the positive electricity moving to the right and disturbing the north pole of the magnetic needle, the negative electricity turning to the left and disturbing the south pole. (Oerstedt.)—One pole of a moveable magnetic needle revolves constantly in one direction round a wire conveying a current of electricity, —and with a different arrangement, the other pole revolves in the contrary direction. (Faraday.) A metallic wire twisted in the form of a helix behaves, while an electric current is running through it, exactly like a magnet, showing a north pole at one end of the helix and a south pole at the other. (Ampère & Arago.)

These effects are best exhibited by voltaic electricity, on account of its greater quantity; but common electricity likewise acts on the magnet, when it is conveyed from the conductor to the wire, not in sparks, but by fine points, or damp threads, or rarefied air. (Colladon, *Pogg.* 8, 336; Nörrenberg, *Zeitsch. Ph. math.* 3; Faraday.) Equal quantities of electricity combining together in the wire in the same time produce equal effects upon the magnet, whatever may be their tension. Hence the deflection of the needle shows the absolute quantity of electricity which is passing through the conductor. (Faraday.)

The *Electrical Multiplier* or *Galvanometer* invented by Schweigger consists of a magnetic needle (or of several needles fastened together with their opposite poles placed over one another) suspended by a delicate thread and surrounded by 100 or several hundred coils of a copper wire covered with silk. By this arrangement, the electric current is made to circulate many times round the needle, and the effects of its several parts become added together, so that a very small quantity suffices to produce deviation. (Schweigger, *Schw.* 31, 1; 32, 320; Oerstedt, *Schw.* 52, 14; Norrenberg, *Zeitschr. Ph. Math.* 3; Becquerel, *Pogg.* 2, 206; Nobili, 8, 338; 20, 213; Nervander, *Ann. Chim. Phys.* 55, 156.)

The electric current, besides its *deviating* or *deflecting* action on the magnetic needle, likewise exhibits a *magnetizing* action: If the wire through which the current passes be twisted in a spiral form round a mass of iron, the latter will become strongly magnetic, as long as the current passes through the wire. Steel likewise retains a part of the magnetism thus developed in it, after the current has ceased. A steel wire also becomes magnetized when placed outside the helix and parallel to it, but the magnetism thus excited is weaker and the direction of the poles is the reverse of that in the former position of the needle. The electro-magnetic action is not prevented by surrounding the needle by a glass tube. (Ampère & Arago.)

2. *Decomposition of Latent Electricity into its two opposite kinds:—Development of Electricity.*

A. *Electricity by Induction.*

When a conductor is charged with one kind of electricity—positive for example—is separated from another containing only latent electricity, by a non-conductor such as air, glass, varnish, &c. the tendency of the positive electricity of the first conductor to combine with the negative electricity of the second causes the latent electricity of the latter to be resolved into its two parts, the negative electricity going towards that part of the second conductor which is nearest to the first, whilst the positive electricity appears in the free state at the other end.

Since, as appears from this, one kind of electricity developes the opposite kind in a body containing only latent electricity, and endeavours to unite with it, it follows that electrified bodies will attract even those in which the electricity is wholly latent. Hence two easily moveable bodies suspended in air appear to repel one another*, because they are attracted by those particles of air which have not yet received any electricity from the bodies, and are therefore in a condition to supply the opposite kind of electricity. This takes place to the greatest extent with those particles of air which are situated beyond the two electrified bodies, and least with those between them.

When the tension of the positive electricity in the first conductor, and of the negative electricity thereby developed in the second becomes sufficiently great, the two electricities make their way through the interposed non-conductor in the form of a spark (the so-called *simple electric spark*), or of a luminous brush, and combine,—and both conductors subsequently contain an excess of positive electricity of less tension than that which previously existed in the first conductor.

If, before this combination takes place, the positive end of the second conductor be connected with the ground by means of another conductor, the positive electricity passes away to the earth, while the negative remains in the second conductor. This is the principle of the *Electrophorus*, the *Condenser*, and the *Leyden Jar*.

B. *Magneto-Electricity.*

If either pole of a magnet be thrust within a metallic spiral connected with a galvanometer, a momentary deviation of the needle will be produced, the north and south poles of the magnet producing opposite effects. If a horseshoe magnet, or a horseshoe-formed keeper belonging to it, be surrounded with silk-covered wire, and the two sharpened ends of this wire amalgamated and made to touch each other loosely,—then, on suddenly pulling the keeper off the magnet, an electric spark will pass between the ends of the wire as they are separated from one another by the jerk. (Faraday.) In the *Magneto-electric Machine* of Pixii, Saxtorph, &c., the horseshoe-formed keeper is surrounded with wire, and the horseshoe magnet is made to rotate rapidly†, so that its two poles alternately approach the two ends of the keeper. The direction of the current in the spiral is reversed with each half-revolution; but by means of the

* The bodies are of course supposed to be similarly electrified. [W.]

† This very clumsy arrangement soon fell into disuse: in all magnecto-electric machines at present used, the magnet is fixed and the keeper revolves. [W.]

Commutator, matters may be so arranged, that, as the electricity issues from the extremities of the spiral, all the positive electricity may be communicated to one conductor, and all the negative electricity to another.

Induction.—Two helices of wire covered with silk, gumlac, or caoutchouc, and wound in the same direction, are placed parallel to each other or one within the other. If now an electric current be passed through one of these helices, the primary helix,—then, at the first instant of its passage, a current in the opposite direction will be developed in the other, the secondary helix: and at the moment when the current in the primary helix ceases, a current will pass through the secondary helix in the same direction as that in the primary helix. If an iron cylinder, or still better, a bundle of thin iron rods covered with silk, be placed within the secondary helix, the current in that helix will be of considerable strength. (Faraday.)

C. *Electricity of Capillarity?*

If one end of the galvanometer wire be connected with a platinum spoon containing a liquid, the other with a pair of forceps holding a porous body, an electric current is set up on dipping the body into the liquid, and continues till the body is completely saturated with the liquid. With hydrochloric or nitric acid and spongy platinum, positive electricity goes from the platinum through the galvanometer to the acid; with nitric or dilute sulphuric acid and charcoal, the current lasts about two hours and travels in the opposite direction. (Becquerel.) In the case of charcoal, chemical action may be supposed to come into play, and likewise in that of the platinum when it has not been very strongly ignited. (Gm.)

D. *Electricity of the Solar Rays?*

When the sun shines on a perfectly dry glass plate, the latter becomes electrical; a second plate on which the light falls after passing through the first does not become so: neither does heating by fire produce electricity. (Matteucci.)

E. *Electricity of Crystals.*

Many crystals, while they are being heated, exhibit opposite electricities at their opposite ends. Those extremities which are positive while the temperature is rising, become negative as the crystal cools; and conversely.

Crystal-electricity is exhibited by: Tourmalin (Æpinus), topaz (Canton), axinite (Beard), boracite, prehnite (both the radiant and fibrous varieties according to Von Kobell, *Kastn. Archiv.* 13, 388), sphene, zinc-glas, and mesotype, (Hauy); (also, according to Brewster, Greenland mesotype, skolezite, and mesolite), rock-crystal, amethyst, tartaric acid, Rochelle salt, and common sugar (Brewster); rhodizite (borate of magnesia, *G. Rose*), neutral tartrate of potash (Hankel), and in a slight degree by milk-sugar (Böttger, *Pogg.* 43, 659). Besides these, the following are enumerated by Brewster as exhibiting crystal-electricity: Diamond, sulphur, sulphate of ammonia, carbonate of potash, chlorate of potash, heavy spar, coelestin, calcspar, fluor spar, sulphate of magnesia, sulphate of magnesia and soda, beryl, iolite, diopside, vesuvian, garnet, analcime, red orpiment, lead-spar, green vitriol, ferrocyanide of potassium, corrosive sublimate, oxalate of ammonia, citric acid, and acetate of lead.—Since, however, Brewster merely examined whether these bodies after

being heated in a flame, exhibited any signs of electric excitement—an effect which might proceed from various causes—the correctness of his statement is doubted by Hankel, who examined most of these substances and found no signs of crystal-electricity in them.

Most of the crystals above enumerated are unsymmetrical, *i. e.*, they exhibit differently formed faces at their corresponding ends. Moreover, Hankel remarks that rock-crystal in the solid state, and neutral tartrate of potash, Rochelle salt, and common sugar in the state of solution, are said by Biot to exhibit circular polarization of light.

Tourmalines are generally more strongly electrical in proportion as they are darker in colour, and have fewer crevices in their interior. (G. Rose, *Pogg.* 39, 320.) Many of them become electrical only when suddenly heated and cooled. Small tourmalines are more easily excited than large ones; and fragments more readily than entire crystals. (Becquerel.) Even the most finely divided tourmaline powder is electrical, so that when warmed it adheres together and to the surface on which it rests. (Brewster.) When a tourmaline is heated, positive electricity appears at that end of the prism which has either a single right terminal face, or merely the three faces of the primitive rhombohedron, or both kinds of faces together,—or in addition, the faces arising by truncation of the terminal edges; and the negative electricity at that extremity which, together with the right secondary plane, has also the three last named faces, or, together with the three faces of the primitive rhombohedron, likewise the three faces of a less obtuse one. (Köhler, *Pogg.* 17, 146.) It is only during heating and cooling that the tourmaline shows signs of electricity; as long as the temperature remains stationary after heating, it shows none; but as soon as the temperature begins to fall, the opposite electrical state is suddenly established. If only one end be heated, that end alone becomes electrical, the electricity diminishing gradually towards the cold end till it is reduced to nothing;—when the heated end is cooled, it acquires the opposite electricity, which gradually diminishes towards the opposite end. If one end is heated while the other is cooled, both exhibit the same kind of electricity. (Bergman, *Opusc.* 5, 402; Becquerel.)

If the end of the tourmaline which exhibits positive electricity when heated, be rubbed with wool, it will become still more strongly electrical, because the friction likewise developes positive electricity; but the opposite end when rubbed with wool does not become electrical, because the positive electricity developed by friction and the negative electricity developed by heat neutralize each other. (P. Erman, *Pogg.* 26, 607.)

In boracite, the four summits of the cube in which the tetrahedral faces are absent become positively electric; the four other diagonally opposed summits, which are replaced by tetrahedral faces, negatively electric. (Köhler.) In the dodecahedrons of rhodizite, the four corners (rhombohedral summits) which have tetrahedral faces become positively electric when heated; the four opposite corners which have no such faces, negatively electric. (G. Rose.)

The short prism of silicate of zinc (electric calamine) is modified at one end by the faces of a rectangular octohedron, at the other by those of a rhombic octohedron; the former becomes positively electric when heated, the latter negatively. (Köhler.)

Brazilian topaz becomes strongly electrical, Siberian slightly, Saxon not at all: when topaz is heated, negative electricity appears at both ends of the prism, and positive on all the lateral faces. (P. Erman.)

Skolezite and mesolite deprived by heat of their water of crystalliza-

tion and reduced to powder, still show signs of crystal-electricity. (Brewster.)

Neutral tartrate of potash crystallizes in right rhombic prisms, but acuminated with two faces at the acute lateral edges, and perpendicularly truncated at the base. The first-mentioned extremity shows negative electricity even when gently warmed, and positive on cooling; the other end exhibits the opposite state. (Hankel.)

The supposition that crystal-electricity proceeds from a structure of the crystal similar to that of the voltaic pile, is contradicted by the fact that the chemical constitution of crystals is homogeneous,—whereas, in the voltaic pile, a mechanical union of heterogeneous substances is essential.

F. *Thermo-Electricity.*

When one part of a metallic circuit is more strongly heated than the rest, an electric current is excited in it under the following circumstances: (*a.*) When the circuit consists of a single metal, and the heating which takes place at a particular part diminishes more rapidly on one side than on the other; and (*b.*) When it consists of two metals, and one of the points of junction is heated.

a. With one Metal.

A metallic wire connected with the two ends of a galvanometer gives no electric current when heated in the middle: but when each end of the galvanometer is connected with a wire, and the end of one of the wires is heated, and then quickly pressed on the cold end of the other, an electric current becomes manifest by the deflection of the needle of the galvanometer. The direction and strength of this current vary with the nature of the metal employed. In the so-called *positively thermo-electric metals* (bismuth, platinum, gold, silver, copper, &c.) positive electricity goes from the cold piece of metal through the galvanometer to the hot piece; in those which are *negatively thermo-electric* (zinc, iron, antimony) from the hot to the cold end. The more one end is heated, the stronger is the current. According to Yelin, bismuth produces the strongest current with a given degree of heating; then follows antimony, then zinc, silver, platinum, copper, brass, gold, tin, and lastly lead; but, according to Nobili, this order is correct for certain temperatures only.

A simple platinum wire connected with a galvanometer also produces a current when heated, if it be tied in a knot at one point and heated near the knot; because the more rapid cooling through the knot causes unequal distribution of heat on the two sides; the positive electricity proceeds from the knot through the galvanometer to the heated part. Two copper wires do not produce so strong a current when clean as they do when covered with oxide or with a thin film of silver or gold, because the covering hinders the communication of heat to the cold end, and consequently interferes with its uniform distribution. (Becquerel.)—Mercury is not thermo-electric, according to Matteucci and De la Rive; very slightly, according to Peltier.

[Many metals, as antimony, iron, and zinc, conduct positive better than negative electricity; others, as platinum, copper, and silver, exhibit the contrary relation. When a metal is heated, its power of conducting electricity diminishes altogether; but the diminution is greatest with regard to that kind of electricity which it conducts least. When a piece of metal heated at the extremity touches a cold piece of the same metal, the heat diminishes gradually from the heated end to the part of

the same piece of metal in contact with the galvanometer, but suddenly, towards the cold end of the other piece of metal. Consequently, in heated platinum, the conducting power is most diminished for positive electricity; since this kind of electricity is least conducted by the platinum when cold; in antimony, the power of conducting negative electricity suffers the greatest diminution. The heat accumulated at one end of the piece of metal endeavours to diffuse itself uniformly through the whole metallic circuit, but can only do so gradually as a whole; its two elements, the two electricities, would flow rapidly round the circuit. Since now the conducting power is different on the opposite sides of the hottest point, the heat is decomposed; and in the case of platinum, the positive electricity goes from the hot end to the cold, and thence into the galvanometer, while the negative electricity goes from the hot piece of metal (which from that cause has less power of conducting positive electricity) into the galvanometer; so that the two electricities recombine and form heat in the colder part of the metallic circuit. With antimony, in which the conducting power is greatest for positive electricity, the direction of the current is the reverse of that just described. This action continues till, by the passage of heat into the cold end, the rate of decrease of the heat becomes the same on both sides of the hottest point, and consequently, there is no longer any inducement for the positive electricity to go one way, and the negative the other; for this reason, no current is produced when a continuous metallic arc is heated at any point whatever.]—*Vid.* p. 316.

Even when the heated end is separated from the cold end by a body in the state of igneous fusion, an electric current is produced in the same direction. If borax, carbonate of soda, carbonate of potash, chloride of potassium, iodide of potassium, sulphate of soda, or chloride of strontium in the state of igneous fusion, be placed between two platinum wires separated by a little distance from one another, and one of the wires be heated more strongly than the other, the positive electricity will go from the colder wire through the galvanometer to the hotter wire. The current is sufficiently strong to decompose iodide of potassium under favourable circumstances. If five platinum wires be joined together by four balls of fused borax, and the four ends of the wires heated always to the right of the borax, a current will be produced sufficient to evolve gas when passed through dilute sulphuric acid. The borax and the other salts suffer no chemical change. Even boracic acid, which conducts less readily than borax, produces a distinct electric current. When the carbonate of soda is not perfectly fused, the direction of the current is reversed. If the platinum wires are separated by glass, the positive electricity passes from the hot platinum through the galvanometer to the cold, when the plate of glass is thin, or when it is thick and strongly heated; but in the opposite direction when the glass is thick and moderately heated. A strongly heated film of mica interposed between the platinum wires likewise allows a little positive electricity to pass from the cold wire through the galvanometer to the hot wire (Andrews).—Also in fused (but not red-hot) phosphate of soda and ammonia, sulphate of copper and potash, anhydrous acetate of soda, nitrate of ammonia, borax, bichromate of potash, acetate of potash, and nitrate of soda, two unequally heated platinum wires produce an electric current, strongest in the first, and weakest in the last-mentioned of these salts (R. Böttger, *Pogg.* 50, 53).—If a hot and a cold platinum wire connected with a galvanometer *be dipped in* water, or if, when the two wires are placed in the same

vessel, hot water be poured on the one and cold on the other, positive electricity will pass for a short time from the cold wire through the galvanometer to the hot wire. (Nobili.)

b. With Two Metals.

When two pieces of different metals connected with a galvanometer are united by soldering or by intimate contact, an electric current is set up, as soon as the point of junction is brought to a temperature different (either higher or lower) from that of the rest of the circuit. (Seebeck.) The strength of the current appears to be in direct proportion to the difference of temperature; its direction depends upon the nature of the metals employed. The metals may be arranged in a *thermo-electric series*, such, that each metal—when connected with the one on its left hand—transmits negative electricity, and when connected with that on its right hand, positive electricity, from its heated point to the galvanometer,—the point of junction being supposed to be heated, and *vice versâ* when it is cooled. The strongest current is produced by a circuit of bismuth and antimony, these metals standing at the extremities of the series.

According to Yelin, the order is: Bismuth, silver, platinum, copper, gold, tin, lead,—zinc, iron, antimony.

According to Becquerel: Bismuth, platinum, lead, tin, gold, silver, copper,—zinc, iron, antimony.

According to Cumming: Galena, bismuth, mercury *and* nickel, platinum, palladium, cobalt, silver alloyed with copper *and* manganese, tin, lead, brass, rhodium, gold, copper, osmium-iridium, silver,—zinc, charcoal, graphite, iron, arsenic, antimony.

The dash separates the thermo-positive from the thermo-negative metals; the conjunction *and* is placed between two metals of equal thermo-electric power. The discrepancies in the statements of different experimenters induce the supposition that the direction of the current is affected by impurities in the metals, and varies with the difference of temperature. That the latter may really be the case, will appear from the following.

When iron is moderately heated in contact with copper, silver, gold, brass, or zinc, positive electricity proceeds from the iron through the galvanometer to the copper, &c., but when the heat is stronger from the copper, &c., to the iron. (Cumming.) The reversal of the direction of the current takes place at a dull red heat, when copper and iron are the metals employed. (Becquerel.)—Zinc and gold produce at 70° a feeble current, which passes from the zinc through the galvanometer to the gold; at 150°, this current ceases; at 180° an opposite current sets in, and becomes very strong at 275°. On the contrary, with zinc and silver at a low temperature, positive electricity passes from the silver through the galvanometer into the zinc. This current attains its greatest strength at 120°, diminishes at a higher temperature, ceases at 225°, and is reversed at still higher temperatures. (Becquerel.)

The farther two metals are separated in the thermo-electric series, and the higher the temperature of their point of junction, the more powerful is the electric current; but it is always small in quantity, and of very feeble tension.

[Since bismuth conducts negative electricity better than positive, and antimony conducts positive electricity better than negative, it follows, from the hypothesis laid down on page 321, that, on heating the point of junction of these metals, the negative electricity will pass through the bismuth, and the positive through the antimony, towards the colder part of the metallic

circuit. When, on the other hand, the point of junction is made colder than the rest of the circuit, heat is decomposed in the warmer part, sending negative electricity through the bismuth, and positive through the antimony, towards the point of junction; hence a reverse current is excited. The effect produced in a circuit of bismuth and antimony is likewise obtained with any other pair of metals, one of which, like platinum or copper, has greater conducting power for positive electricity, the other, like zinc or iron, for negative electricity. In the case of two metals, both of which conduct one kind of electricity—*e. g.*, negative electricity—better than the other, it must be observed that this power belongs to the two metals in different degrees, *e.g.*, to bismuth more than platinum, and to platinum more than copper. In such a case, the negative electricity will always travel through that metal which has relatively the greater power of transmitting it, and the positive electricity through the other, which relatively offers it the least resistance. The reversal of the direction of the current at certain temperatures seems to imply, that the power of a metal to conduct one kind of electricity in preference to the other varies with the temperature.]

By combining a number of thermo-electric pairs into a *thermo-electric Battery, Chain,* or *Pile,* a powerful thermo-electric current may be obtained: *e. g.*, a number of bars of bismuth and antimony, or of platinum and iron, alternately soldered together, and heat applied to the first, third, fifth, &c., points of junction, whilst the second, fourth, &c., are kept cold. In this manner, the thermo-electric current produces, not only deflection of the needle, but likewise chemical decompositions of liquids (Botto, *Pogg.* 28, 238), and heating effects,—so that even when one of the conducting wires of the battery is cooled by immersion in ice, the point of junction of that wire situated without the ice becomes sensibly warmed. (Watkins, *Phil. Mag. J.* 14, 82; also *Pogg.* 46, 497.)—Melloni's *Thermo-multiplier* or *Thermoscope* (p. 214) is also a pile formed in this manner of bars of bismuth and antimony, and connected with a galvanometer. The rays of heat fall on the 1st, 3rd, 5th, &c., points of junction, whilst the 2nd, 4th, &c., are kept cool. The smallest difference of temperature between the two sets of junctions suffices to produce deviation of the needle.

A thermo-electric pile of bismuth and antimony, which exhibited no action on the magnet, when heated, acquired this power permanently when previously dipped for a second in nitric acid of 1·4 specific gravity. (Döbereiner, *Pogg.* 49, 588.)

G. *Electricity by Friction: Common Electricity.*

Solid bodies become oppositely electrified when rubbed on one another, and to a certain extent when merely pressed together and afterwards separated. Homogeneous bodies for the most part exhibit this result only when their surfaces are in different states, or when they differ in temperature; with heterogeneous bodies, the development of electricity is much greater.

When two parallel faces, natural or artificial, of a mineral are pressed between the fingers, the mineral frequently becomes electrical on these surfaces, generally showing positive electricity. Calcspar retains the electricity developed from three to eleven days, topaz and fluor-spar several , mica one or two hours, and rock-crystal for a shorter time. Talc be insulated in order to render it electrical; heavy spar and gypsum ot sensibly electrified. (Hauy.)—According to Becquerel, not a trace

of electricity is perceptible while bodies are being pressed together; it is not till they are separated, that the one appears positively, the other negatively electrified. A slice of cork becomes positively electrified when pressed against a slice or plate of caoutchouc, orange-peel, retinasphalt, coal, amber, zinc, copper, silver, cyanite, or heated double refracting spar, these substances at the same time becoming negative. On the contrary, the slice of cork becomes negative with all dry animal substances, with heavy spar, gypsum (which must be freed by drying from hygroscopic water), fluor-spar, and double refracting spar, not heated,—those substances at the same time becoming positive. Two good conductors pressed together exhibit, when separated, no other electricity than that developed by mere contact. Two similar bodies do not become electrical by pressure unless one of them is at a higher temperature than the other; and then the hotter body always becomes negative, the colder positive. The strength of the electricity thus developed depends upon the nature of the bodies, the state of their surfaces, the intensity of pressure, and the rapidity of separation. Cork produces more electricity with calcspar, when the pressure is exerted on one of the faces parallel to the cleavage-planes, than with heavy spar, with the latter more than with polished rock-crystal, and with this more than with gypsum, or with the polished surface of calcspar, and—when pressure, temperature, dryness, and polish, of the cleft surfaces are equal,—three times as much with calcspar as with gypsum. The intensity of the electricity varies directly as the pressure,—so that when the latter is doubled, the former is doubled also. Lastly, if the two bodies which have been pressed together are slowly separated, the two electricities have time to reunite, and a much smaller quantity remains in the free state after the separation. Bodies rendered electrical by pressure retain the electricity for a longer time, in proportion as their insulating or non-conducting power is greater.

These phenomena are ascribed by Becquerel to the same cause as that which produces the following effects, observed by himself. When two laminæ of a crystal of mica are suddenly torn asunder, there is not only an appearance of light produced, but one lamina becomes positively, the other negatively electrified: if again pressed together and subsequently separated, they again appear electrified. Also, on the cleavage of calcspar, fluor-spar, heavy spar, topaz, talc, and dry warmed gypsum, and on tearing a playing-card into its two sheets, the separated laminæ appear oppositely electrified. In topaz, whose cleavage takes place parallel to the terminal faces of the prism, the cleft surface belonging to one end of the prism exhibits, sometimes one kind of electricity, sometimes the other. When melted shellac is poured upon glass and pulled off after cooling, both become electrified.

Non-crystalline bodies, such as sealing-wax or glass, exhibit no electricity when broken. (*Vid. Crell. Ann.* 1786, 1, 325.) In the former cases, the separation of bodies united by pressure produced electricity; in the present case, it is a union produced by cohesion that is overcome. (Becquerel.)

If sulphate of copper and potash be brought into a state of red-hot fusion in a platinum crucible—connected, by a ring of wire on which it rests, with a Bohnenberger's electrometer—and then left to cool, no electricity will be apparent during the crystallization; but as soon as the crystalline mass begins to contract with an audible decrepitation, and falls to pieces gradually and spontaneously, the formation of each new fissure is accompanied by a development of electricity, and the effect goes on till

the whole mass is crumbled into dust. (R. Böttger, *Pogg.* 50, 43.)—Two sheets of unsized paper, impregnated with hot wax, stick fast together when rubbed with a leather cushion; and, on being pulled asunder while warm, are found to be electrified sufficiently to produce a spark. (Simon, *Br. Archiv.* 31, 216.)

According to Hauy, the following substances become positively electrical when rubbed with woollen cloth, and are likewise insulators: Diamond, sulphate of potash, nitre, common salt, witherite, heavy spar, strontianite, double refracting spar, arragonite, apatite, anhydrite, gypsum, glauberite, fluor-spar, boracite, bitter spar, sulphate of magnesia, sapphire, spinell, chrysoberyl, quartz, zircon, emerald, euclase, topaz, iolite, cyanite, chiastolite, axinite, tourmalin, garnet, cinnamon stone, vesuvian, felspar, prehnite, mica, apophyllite, hornblende, actynolite, tremolite, augite, diopside, epidote, nephelin, mesotype, stilbite, analcime,—and, in short, probably all combinations of earths, alkalis, and mineral acids among themselves occurring in the mineral kingdom, with the exception of talc: moreover, electric calamine, zinc-spar, tinstone, lead-spar, sulphate of lead, sphene, and tungstate of lime.—The following become positively electric, and are conductors: Bismuth, zinc, lead, copper, brass, silver, and silver-amalgam. Non-conductors becoming negatively electrical, are: Sulphur, talc, anatase, titanschorl, uranite, cobalt-bloom, orpiment, blende, phosphate of lead, molybdate of lead, chromate of lead, specular iron, green vitriol, prussian blue, cube-ore, red oxide of copper, malachite (which sometimes becomes positive), blue carbonate of copper, pseudo-malachite, blue vitriol, dioptase, chrysocolla, arseniate of copper, cinnabar, subchloride of mercury or horn-quicksilver, red silver, amber, retinasphalt, elastic petroleum (Erdharz), honey-stone, and anthracite.—Conductors becoming negatively electrical are: Ilvaite, allanite, tantalite, yttro-tantalite, wolfram, sulphuret of molybdenum, chrome iron ore, pitch-blende, peroxide of manganese, sulphuret of manganese (mangan-glanz), earthy cobalt, arsenic, antimony, native sulphuret of antimony, black tellurium, bismuth-glance, tin, tin-pyrites, galena, iron, graphite, magnetic iron ore, red hæmatite, magnetic pyrites, native ferroso-ferric sulphate, iron pyrites, arsenical pyrites, copper-glance, grey copper, nickel, copper-nickel, native amalgam of tin, vitreous silver, antimonial silver, gold, platinum, and palladium.—When the crystalline structure is imperfect, the property of becoming electrical by friction is often absent, and so likewise is the insulating power; *e. g.*, calc-spar and statuary marble. Want of polish on the surface also frequently interferes with the insulating power, and produces negative instead of positive electricity, when the substance is rubbed, *e. g.*, in quartz.

Insulated metals rubbed with the dry hand, or with horn, ivory, wood, or cork, become electrical,—rhodium, platinum, palladium, gold, cobalt, nickel, tellurium, and antimony, always negative, the last very strongly,—silver, copper, brass, and tin, mostly negative; zinc and iron, sometimes negative, sometimes positive; lead and bismuth (the latter in the highest degree) positive. It is to be supposed that all metals, if perfectly clean, would become negative; but since the more oxidable soon become covered with a thin film of oxide, a portion of this oxide often adheres to the rubber, and the metal becomes positive by being rubbed with it; or, if the film of oxide holds faster, the friction takes place between this oxide and the wood, &c., in consequence of which, the metal becomes negative. Freshly polished metals rubbed with new wood always become negative, except lead and bismuth, which are sometimes rendered positive. (De la Rive.)

On rubbing together two metals connected with the ends of the galvanometer, the following order is observed, beginning with the metal which is negative with all others: Bismuth, nickel, cobalt, palladium, platinum, lead, tin, gold, silver, copper, zinc, iron, cadmium, antimony. This is the thermo-electric series. Nevertheless, Becquerel is of opinion (wrongly perhaps) that the production of electricity in this manner cannot be attributed to the heat developed by friction.—A button of bismuth, antimony, iron, or platinum, rubbed on a plate of the same metal, becomes positive; zinc likewise exhibits this action in a slight degree. Filings or granules of metal, as well as metallic oxides or sulphurets, let fall on a plate of the same metal placed in a slanting position, always become negative; so likewise does rough glass when rubbed upon smooth. (Becquerel.)—To this class of effects belongs also the electrization of powders let fall through sieves made of different materials.

Finely-divided copper, obtained by reducing carbonate of copper by means of hydrogen gas at a very low temperature, becomes strongly electrical when pressed together.

Perfectly dry oxalate of lime becomes positively electrified, in so high a degree, merely by stirring it with a rod of glass or platinum (which at the same time becomes negative), that the powder is lifted out of the basin which contains it. (Faraday, *Qu. J. of Sc.*, 19, 338.)

Sulphur, wax, tallow, cocoa, or chocolate, after fusion, and calomel after sublimation, left to cool in a glass or metallic vessel, shows no sign of electricity on its upper surface; but very strong electrization, often sufficient to give sparks, on the surface which has been in contact with the vessel. The electricity is generally positive; but with sulphur I have sometimes found it to be negative, whilst the inner surface of the vessel exhibits the opposite electricity in an equal degree. (*Vid. Crell. Ann.* 1784, 2, 119; 1786, 1, 325; *Gilb.* 23, 230; *Kastn. Archiv.* 6, 472.) These phenomena were formerly attributed to the existence of positive electricity in a state of combination in liquids, this positive electricity being supposed to be set free on the passage of the body to the solid state. But since the positive electricity does not show itself on the upper surface of the solidified mass, but only where it is in contact with the vessel,—and since, according to Gay-Lussac (*Ann. Chim. Phys.* 8, 159), no negative electricity is set free during the fusion of metals in glass vessels,—which, however, ought to ensue if positive electricity were rendered latent during the liquefaction,—it is better to suppose, with Gay-Lussac, that the electricity observed in this process proceeds merely from the friction occasioned by the unequal contraction of the solidifying body and of the glass vessel with which it is in contact, and from a partial separation resulting from the same cause.

The following experiments, however, cannot well be explained on such a supposition. When water is allowed to freeze in a Leyden jar, the inside of the jar becomes slightly positive, the outside slightly negative; the rapid deposition of ice in the form of hoar-frost produces the contrary effect. (Grotthuss, *Ann. Chim. Phys.* 27, 111.)—If a glass bulb and a tube about 0·01 or 0·02 metre long attached to it be completely filled with water, surrounded with cotton moistened with ether, and placed under the receiver of the air-pump, an electric spark, visible even by day, will dart out of the tube the moment before the liquid freezes. (Pontus, *J. Chim. Med.* 9, 430.)

The degree and kind of electricity which two bodies assume on being rubbed together vary with the temperature, the pressure, and the hygro-

metric state of the air. (Dessaignes, *J. Phys.* 82, 360 and 413; 83, 4, 194 and 415.)—A glass tube rubbed with a cloth perpendicularly to its axis becomes positive; but when pressed under the arm and rubbed backwards and forwards, parallel to its axis, it generally becomes negative. (Gm.)

According to Wollaston's view, friction-electricity always proceeds from oxidation: for, according to that philosopher, glass gives no electricity when rubbed with an amalgam of silver or platinum, because these metals are not oxidable. It is more powerfully excited by zinc-amalgam than by tin-amalgam, because the former is the more oxidable; and still more strongly by a mixture of the two, which oxidates most quickly of all. According to Wollaston, also, an electrical machine gives no electricity when made to work in carbonic acid gas. But, according to Gay-Lussac, electricity is obtained in carbonic acid gas when the gas is dry; according to Sir H. Davy, it is also obtained in hydrogen gas, and more abundantly in carbonic acid gas than in the air; and, according to Peclet (*Ann. Chim. Phys.* 70, 83), the electric excitement is equally strong in dry air, carbonic acid gas, and hydrogen gas.

On the development of electricity by friction depend the *Electrophorus* and the *Electrical Machine*, which yield electricity of the greatest tension, *i. e.* accumulated in the greatest quantity on a given surface.

H. *Development of Electricity by Chemical Changes in Ponderable Bodies: Chemical Electricity.*

a. By Chemical Combination.

During the combination of two substances, a very small quantity of electricity often shows itself in them. In oxygen which combines with combustible bodies, and in acids which combine with salifiable bases, the electricity is positive; in combustible bodies and salifiable bases it is negative.

[Oxygen contains positive electricity in a state of combination, combustible bodies negative electricity. When these ponderable bodies combine, their opposite electricities also come together in the form of fire; but under certain circumstances, a very small quantity of them appears to remain uncombined, so that a trace of positive electricity shows itself on the side of the oxygen, and a trace of negative electricity on the side of the combustible body. This is also Pouillet's view, as far as combustions are concerned. Similarly, with acids and salifiable bases.]

To render this feeble electricity sensible, one of the bodies must be placed in connection with the upper plate of the condenser of a Bohnenberger's electroscope, and the other with the ground; or else the two bodies must be respectively connected with the two ends of the galvanometer.

When coals are burnt in the air, negative electricity accumulates in the vessel in which the combustion takes place. (Lavoisier & Laplace.) An insulated stove in which a strong coal fire is burning, becomes negative; the electricity is strongest at each addition of fuel. (Williams, *Phil. Mag. J.* 18, 93.)

If a cylinder of charcoal, burning only at the upper end, be placed on the cover of the condenser, negative electricity soon accumulates in the condenser; to a still greater degree when the combustion is fed with oxygen gas. If the burning cylinder be connected with the ground, and *a metal plate* communicating with the cover of the condenser be held

over it at the distance of a few inches or a foot, the condenser will become positively electrical. If the charcoal cylinder burning at one end be laid horizontally, or if it be placed upright and made to burn at the side instead of on the top, no electricity will be perceptible, because the negative electricity of the charcoal will be neutralized by the positive electricity of the surrounding air. (Pouillet.)

When hydrogen gas issuing from a metal tube is set on fire, the cover of a condenser connected with the tube becomes negative. If the tube be connected with the ground and a metal plate held at some little distance above the flame, the plate conveys positive electricity to the plate of the condenser. When the hydrogen issues from a glass tube, negative electricity is obtained by introducing into the middle of the flame a narrow coil of platinum wire connected with the condenser; but if the coil be wide enough to surround the flame without touching it in any part, the electricity will be positive. A metal plate held over the flame does not become electrical when the gas is burned from a glass tube,—because the glass insulates, and consequently, the two electricities neutralize one another within the flame. The flame of alcohol, ether, oil, tallow, or wax, exhibits the same effects as that of hydrogen gas. (Pouillet.) In the combustion of alcohol in the lamp without flame, negative electricity also accumulates in the spiral wire, and positive electricity in the surrounding air. (Becquerel.)

Pfaff (*Pogg.* 51, 110) regards these statements as erroneous, and asserts that not a trace of electricity is apparent in the combustion of hydrogen gas, phosphorus, sulphur, zinc, alcohol, or ether; only in the combustion of charcoal is there an indication of negative electricity; but as no positive electricity can be detected in the carbonic acid which rises from it, he regards the phenomenon as proceeding from thermo-electricity.

A thin copper tube through which a dry mixture of chlorine gas and air is passed becomes negative; the gas subsequently transmitted through a platinum tube renders it positive.

On connecting the ends of the galvanometer with two iron wires, *a* and *b*, inserting *a* into a piece of charcoal, then heating to redness both the charcoal with the end of the wire *a* enclosed in it, and also the extremity of the wire *b*, and connecting the latter with the charcoal, a strong current will pass from the wire *b* through the galvanometer to the wire *a*; hence, in this case, the carbon acts the part of oxygen [*i.e.* in its combination with the iron of *a*, positive electricity is set free in it, and negative electricity in the iron]. (Becquerel.)

For the investigation of the development of electricity in the combination of two liquids, or of a liquid and a solid, the pieces of apparatus represented in Plate IV are useful.

App. 1. A platinum spoon containing a liquid is connected with one end of the galvanometer. With the other end is connected a pair of platinum forceps, in which a solid body can be fastened so as to dip into the liquid.

App. 2. Two cups or beakers *a*, *b*, into which are plunged the platinum terminations of the galvanometer, contain two different liquids which are connected with one another, either by a bunch of asbestus or cotton-threads, or by means of a siphon, filled, sometimes with one of the liquids, sometimes with a liquid different from both.

App. 3. A beaker glass is cut in halves in a vertical direction, and after a sheet of bibulous paper has been inserted into it, bound tightly together again. Into the two divisions formed by the paper partition two

different liquids are poured, and the platinum ends of the galvanometer dipped into them.

App. 4. The lower part *h* of a U-tube is stopped up with cotton, asbestus, or clay, moistened with a suitable liquid; then the arm *a* is filled with this same liquid and the arm *b* with another.

App. 5. The extremity *b* of the U-tube being stopped with the finger, the arm *a* is filled with the heavier liquid; the end *a* is then closed, the end *b* opened, and the lighter liquid carefully poured in at this end, so that it may dispose itself in a separate stratum above the heavier liquid.

App. 6. A hole having been made in the bottom of a beaker-glass, and one of the platinum ends of the galvanometer cemented into it, the two liquids are carefully introduced into the glass, one above the other, and the other platinum termination made to dip into the upper liquid.

App. 7. A glass tube *a* has its lower extremity either tied round with a bladder or stopped up with clay moistened with a liquid. It contains a liquid, and dips with its lower end into another liquid contained in the beaker *b*. Into *a* and *b* the platinum ends of the galvanometer are made to dip.

App. 8. Two glass tubes *a*, *b*, closed at the bottom with bladder or moistened clay, are filled with different liquids; and made to dip by their lower ends into the liquid in the dish *c*.

Acids with Acids. The platinum spoon (*App.* 1) containing oil of vitriol, and the spongy platinum in the forceps, nitric acid, positive electricity goes in considerable quantity from the oil of vitriol through the galvanometer to the nitric acid. If the oil of vitriol be previously diluted with one-half water a strong current is set up in the opposite direction. In the former case, the action of the oil of vitriol on the water of the nitric acid probably comes into play. (Becquerel.)—From oil of vitriol (*App.* 2) positive electricity passes in small quantity through the galvanometer to nitric acid. (De la Rive.)—Positive electricity goes from phosphoric acid, through the galvanometer, to sulphuric, hydrochloric, or nitric acid; negative from nitric to hydrochloric, hyponitric, or acetic acid. (Becquerel.)—Positive electricity goes from oil of vitriol, through the galvanometer, to concentrated hydrochloric acid (*App.* 2 or 7); on the contrary, from concentrated nitric acid to oil of vitriol (*App.* 2 or 7). *Walcker.*—Positive electricity goes in large quantity from slightly diluted oil of vitriol through the galvanometer to nitric acid. (*App.* 5.) *Mohr.*

Concentrated Acids with dilute Acids. From concentrated sulphuric or hydrochloric acid, positive electricity goes through the galvanometer to the same acids in a state of dilution. (*App.* 2 or 7.) *Walcker.*—From concentrated nitric acid, a feeble current passes through the galvanometer to dilute nitric acid, diminishing in intensity as the 2 liquids are moved about at their surface of contact. (*App.* 5.) *Faraday.*

Acids with Water. From concentrated sulphuric or nitric acid contained in the spongy platinum in the forceps (*App.* 1), positive electricity goes through the galvanometer to water in the platinum spoon,—weak at first, but continually becoming stronger, as the water by taking up acid becomes a better conductor,—then gradually diminishing in force, till the liquids have become completely mixed, when it stops. With hydrochloric acid and water, the current takes the opposite direction; so likewise with boracic, oxalic, and citric acid, which are fixed in the forceps in the solid state. (Becquerel.)—With sulphuric acid and water or ice, positive electricity passes from the water through the galvanometer to the acid. *(Nobili.)*

Acids with Salts. Positive electricity goes from phosphoric acid, through the galvanometer, to solutions of all salts; from nitric acid to solutions of sulphates, chlorides, and nitrates (Becquerel);—from nitric acid to solution of nitre. (H. Davy).—Positive electricity goes from sulphuric acid, through the galvanometer, to the sulphates of potash, copper, and red oxide of mercury; from hydrochloric acid to chloride of potassium, sodium, barium, or calcium, and from nitric acid to nitre: always therefore from the acid through the galvanometer to the salts of the same acid; positive electricity also goes from hydrochloric acid through the galvanometer to sulphate of magnesia or nitre. (Nobili.) —The current goes from dilute sulphuric acid through the galvanometer to sulphate of zinc or copper, and from concentrated nitric acid to sulphate or nitrate of copper. On the contrary, from chloride of mercury to oil of vitriol, from nitrate of silver to acetic acid, and from chloride of gold to hydrochloric acid. (*App.* 2 or 7.) *Walcker.*

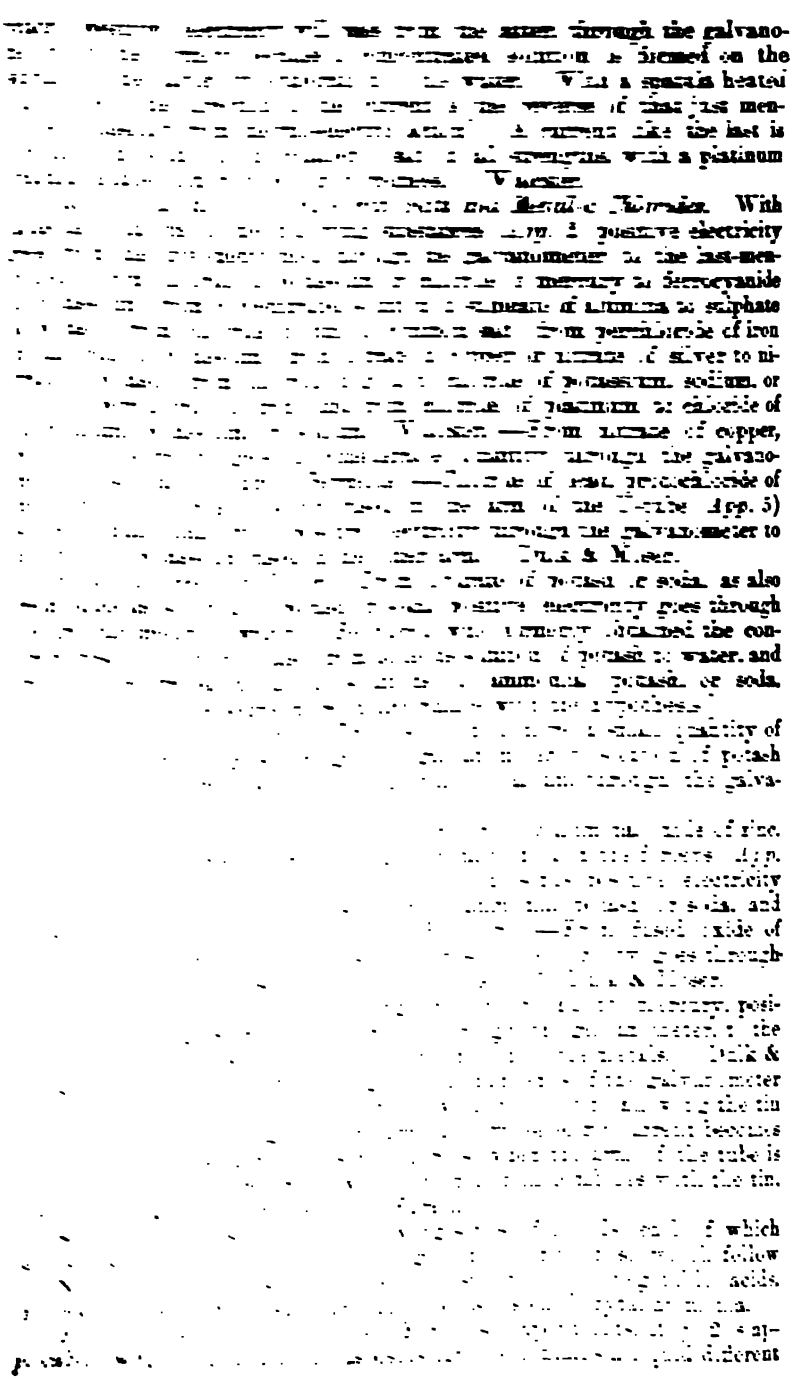
Acids with Salifiable Bases. Positive electricity goes from dilute sulphuric, hydrochloric, or nitric acid, contained in the platinum spoon, (*App.* 1) through the galvanometer, to moistened hydrate of potash in the forceps. Similarly, from dilute acids to aqueous solution of potash (*App.* 2, with asbestus.) Becquerel.—Walcker also obtained a strong current from the acid (but probably through the galvanometer?) to the potash. Faraday, on the other hand, obtained no current with dilute sulphuric acid and aqueous solution of potash (*App.* 3); Mohr also obtained with dilute sulphuric or hydrochloric acid, on the one side, and aqueous solution of potash or ammonia on the other, either no current at all, or merely a slight disturbance of the needle at the commencement of the action; whereas, he found that from concentrated or dilute nitric acid, positive electricity goes through the galvanometer to the potash.

From sulphuric or nitric acid, positive electricity goes through the galvanometer to aqueous solution of ammonia (Nobili); from dilute sulphuric acid to aqueous ammonia, soda, or baryta (*App.* 2 or 7) *Walcker;* from sulphuric, hydrochloric, or nitric acid, through the galvanometer, to solid lime; but, on the contrary, from lime-water through the galvanometer to the acid. It also goes from solid lime through the galvanometer to aqueous solution of arsenic, oxalic, or tartaric acid, and from aqueous ammonia to oxalic acid. (Nobili.)

If hydrated phosphoric acid be fused in one arm of the U-tube, (*App.* 5) and hydrate of potash or oxide of lead in the other, positive electricity goes from the acid through the galvanometer to the base (especially with potash) in sufficient quantity to produce a slight decomposition of iodide of potassium. (Dulk & Moser, *Pogg.* 42, 91.)—From nitric acid, positive electricity goes through the galvanometer to oxide of lead. (Faraday.)

Salts with Water. When sulphate of soda or chloride of barium is dissolved in water, a feeble positive current goes from the water through the galvanometer to the salt. (Becquerel.) From a solution of nitrate of silver in 12 times its weight of water positive electricity goes through the galvanometer to pure water. (Fechner.)

Concentrated with dilute saline solutions. Positive electricity goes from a concentrated solution of common salt or nitre, through the galvanometer, to a dilute solution of the same. (*App.* 2.) *Becquerel;* also from dilute to concentrated solution of liver of sulphur, through the galvanometer. (Faraday.)—If two platinum spatulas, one cold and the other red-hot, be dipped into the same solution of 1 part of common salt in 10 parts of



from those in the two vessels; and *App.* 9, when the three vessels and the siphon or threads are filled with different liquids.

If *a* (*App.* 9) contains nitric acid, *c* soda, and *b* nitric acid, *c* being connected with *b* by a siphon filled with nitre, and *a* with *b* by a bundle of asbestus, positive electricity goes from *a* through the galvanometer to *b*, and is more than doubled in quantity when hydrate of soda is placed upon the asbestus. A similar result is obtained when hydrochloric or sulphuric acid is used instead of nitric acid, and common salt instead of nitre. (Becquerel.) [The current excited by the acid between *a* and *c*, the direction of which is from *a* to the galvanometer, is not completely neutralized by the two opposite currents produced by the action of the acid in *c* on the saline solution in *i*, and of the latter on the soda in *c*.]

If *a* (*App.* 2) contains nitric acid, *b* concentrated solution of potash, and the cotton-wick, *h*, solution of Glauber's salt, about twice as much positive electricity goes from the acid through the galvanometer to the potash, as would be set in motion, if *a* contained nitric acid, and *b* and *h* Glauber's salt, — or *a* and *h* Glauber's salt, and *b* potash. [In the first case, the two currents produced by the acid acting on the Glauber's salt, and this on the alkali, assist each other; in the other two, one only of these currents is produced.] If the first experiment lasts some time, and the threads *h* are not above three inches long, the deflection of the needle increases suddenly from 5° to 20°, when the acid comes into immediate contact with the potash. The acid and alkali come most quickly into contact in the wick when the latter contains the salt which is produced by the combination of the two, *e. g.*, nitre in the case of nitric acid and potash, and Glauber's salt in that of sulphuric acid and soda; if, on the other hand, the wick contains pure water, the infiltration takes place very slowly: no deflection is produced at first, but after about twelve minutes, a strong deflection of 20°. When the wick is six inches long, no increase of the current takes place, even if it contains a saline solution; on the contrary, the current becomes gradually weaker; because, after a time, no more chemical combination takes place in the wick. The deflections of the needle produced at the commencement of the action are as follows,—it being observed that the first-named substance is placed in the vessel *a*, the second in the wick *h*, and the last in the vessel *b*,—and that in each case, the positive electricity goes from the first substance, through the galvanometer, to the last-named:—With nitric acid, Glauber's salt and potash, 5°;—nitric acid, Glauber's salt, Glauber's salt, 3°;—Glauber's salt, Glauber's salt, potash, 3°;—nitric acid, nitre, potash, 4°;—nitric acid, nitre, nitre, 2°;—nitre, nitre, potash, 2°; a mixture of 2 measures of oil of vitriol with 1 measure of water, Glauber's salt, soda, 5°;—the same mixture, Glauber's salt, Glauber's salt, 3°;—Glauber's salt, Glauber's salt, soda, 2°;—mixture of 2 measures of oil of vitriol and 1 water, nitre, soda, 12°;—the same mixture, nitre, nitre, 5°;—nitre, nitre, soda 3°;—the same mixture of oil of vitriol and water, sal-ammoniac, soda, 16°;—the same mixture, sal-ammoniac, sal-ammoniac, 6°;—sal-ammoniac, sal-ammoniac, soda, 6°. (De la Rive.)

If the vessels *a*, *b*, (*App.* 9) are filled with solution of nitre, and the wicks *g*, *i*, saturated with it—the vessel *c* containing nitric acid, and a piece of hydrate of potash being placed upon the wick *i* at *x*, where it dips into the nitric acid—a current is set up from the nitric acid through the galvanometer to the hydrate of potash, much stronger than that which is produced by the use of aqueous solution of potash,—because the former becomes more heated by combining with the nitric acid;—and, generally

speaking, the current goes constantly from the colder body to that which is most heated during the combination: moreover, the phenomenon is thermo-electric [?]. (Nobili.)

Fechner, proceeding upon the contact-theory—according to which metals excite an electric current, even in liquids which do not act chemically upon them—endeavoured to get rid of the effect which, according to this view, might be expected to arise from dipping the platinum terminations of the galvanometer into two different liquids, by immersing these platinum terminations in two cups, *a*, *b*, (*App.* 10) containing the same liquid—placing the two liquids whose mutual action was to be investigated, in two other cups, α, β, and connecting the four cups by three siphon-tubes. The siphons *g*, *i*, contained the same liquid as the cups *a*, *b*; the siphon *h* either the liquid in α or that in β. [By this arrangement, a complicated action is always obtained: not only is a current produced by the mutual action of the liquids in α and β, but likewise by that of the liquid in *a* upon that in α, and of the liquid in *b* on that in β; and the direction and strength of the current is the resultant of the sum or difference of these three actions.] The following are some of the numerous results obtained in this manner:—the liquid in the cup α is always that from which positive electricity passes through the galvanometer to the cup β.

Glauber's salt in *a*, *b*, sulphuric acid in α, potash in β.—Common salt in *a*, *b*, potash in α, hydrochloric acid in β.—Spring water or nitric acid in *a*, *b*, nitric acid in α, potash in β.—Nitre in *a*, *b*, potash in α, sulphuric acid in β;—Nitre in *a*, *b*, sulphuric acid in α, nitric acid in β.

In the following experiments of Fechner, the three liquids,—solution of potash, nitric acid, and solution of nitre,—were distributed in various ways among the 4 cups, and the following deflections were obtained.

1. Nitre in *a*, *b*, nitric acid in α, potash in β; positive electricity goes from *a* through the galvanometer to *b*, deflecting the needle 40°. [The principal current is excited by the action of the nitric acid on the potash; but the two more feeble currents produced by the action of nitric acid on nitre and potash on nitre, take the direction opposite to that of the first and weaken it.]

2. Potash in *a*, *b*, nitric acid in α, nitre in β; positive electricity goes from *b* through the galvanometer to *a*; deflection 33°. [In this case also the principal current produced by nitric acid and potash between *a* and α, which, according to the arrangement, must take the opposite direction to that in 1, is weakened by the two currents produced by nitric acid and nitre, and by potash and nitre, in the same degree as in 1; hence the deflection is nearly the same.]

3. Nitric acid in *a*, *b*, potash in α, nitre in β; positive electricity goes from *a* through the galvanometer to *b*: deflection 48°. [Here again the two feebler currents weaken the principal current; hence the deflection is about the same.]

4. Nitric acid in *a*, potash in *b*, nitre in α and β; positive electricity goes from *a* through the galvanometer to *b*, producing a deflection of 140°, which lasts much longer than in the former cases. [In this case, positive electricity goes from the nitric acid through the galvanometer to the nitre, and likewise from the nitre through the galvanometer to the potash; the united action of these two feebler currents produces a deviation greater than that which results from the action of a principal current weakened by two feebler currents.]

5. *Nitric acid in a,* nitre in *b*, potash in α and β; positive electricity

from a through the galvanometer to b; deviation 164°. [The principal current produced by the action of the acid on the potash is opposed only by the feebler current resulting from the mutual action of potash and nitre.]

6. Potash in a, nitre in b, nitric acid in α and β; positive electricity goes from b through the galvanometer to the potash, producing a deviation of 168°. [Here again the principal current produced by the action of potash and nitric acid is counteracted only by the feebler current resulting from nitric acid and nitre.]

Becquerel's Oxygen-circuit. A glass tube (*App.* 11) is closed at its lower extremity with clay moistened with a concentrated solution of potash; the tube is then filled with strong potash-solution and its lower part dipped into a vessel filled with strong nitric acid. If now the platinum ends of the galvanometer be immersed in the two liquids, a large quantity of oxygen gas will be developed on the surface of the platinum in the potash (it may be most conveniently collected by having the platinum wire which dips into the potash cemented into a glass tube open at the bottom, this tube being afterwards filled with potash and inverted), and nitrous acid will accumulate in the nitric acid, colouring it first green and then blue: at the same time, positive electricity will pass from the acid through the galvanometer to the potash. The action continues for several days. But the electric current is very feeble in comparison with the copious evolution of gas; it is sufficient indeed to separate copper, when passed through a solution of blue vitriol, but not to heat fine platinum wire. (Becquerel.) Jacobi likewise obtained a large quantity of oxygen gas, and at the same time an electric current which decomposed iodide of potassium, but not sulphate of copper.—Moser & Dulk (*Pogg.* 42, 91) who obtained a remarkably large quantity of oxygen gas, found, contrary to Becquerel's statement, that the electric current thus excited produced cold as well as heat in Peltier's apparatus.—Mohr obtained no oxygen gas with this apparatus, and Pfaff only a few bubbles in several hours. These negative results, possibly arising from differences of manipulation or in the materials employed, cannot be considered of equal weight with the often verified statement of Becquerel,—however enigmatical it may appear that a chemical action accompanied by so copious an evolution of oxygen gas, should produce a current so feeble in comparison. It may perhaps be suspected that if the clay be moistened with a solution of common salt or of potash containing chloride of potassium,—nitrous acid and chlorine, together with a salt of nitric acid, may be produced by the action of the nitric acid on the chloride of sodium or potassium,—the nitrous acid going over to the nitric acid, while the chlorine, taking the opposite direction, converts the potash into chloride of potassium and oxygen gas. I have however satisfied myself that, even when the nitric acid and potash are perfectly free from chlorine, oxygen gas (capable of igniting a glowing slip of wood and condensing with nitric oxide gas) is abundantly developed.

If the nitric acid in Becquerel's apparatus be replaced by a mixture of 2 parts oil of vitriol and 1 part water, only a small quantity of oxygen gas is evolved on the platinum immersed in the potash, and a little hydrogen on the platinum in the acid,—an electrical current being also produced in the same direction, capable of decomposing, not only iodide of potassium, but also sulphate of copper. (Becquerel.) Mohr obtained with the same arrangement neither gas nor electric current. I have also tried the experiment with the same clay and potash that were used

speaking, the current goes constantly from the colder body to the
is most heated during the combination: moreover, the
thermo-electric [1]. (Nobili.)

Fechner, proceeding upon the contact-
metals excite an electric
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stomach of an animal, the other the gall-bladder or the inside of the liver,
a deflection of the needle is produced, twice as great as in the preceding
experiment,—continuing after the death of the animal, and only diminish-
ing a little because the fluids are no longer renewed. Even when the
stomach and liver are taken out of the animal, the same action is pro-
duced. Similar currents are also excited between stomach and spleen or
urinary bladder, and between bladder and intestines; on the contrary, no
currents are produced between the two kidneys, between two pieces of the
small intestines, or between the liver on the one side, and the pancreas,
spleen, or intestines on the other. (Donné, *Ann. Chim. Phys.* 57, 405.)

Similar currents are also excited in plants. If one extremity of the gal-
vanometer be inserted into the stalk of an apple or pear, the other into the
opposite end of the axis, positive electricity passes from the latter through
the galvanometer to the stalk. In peaches and apricots, the electric
current takes the contrary direction: but no current is excited when the
ends of the galvanometer are inserted into the fruit at right angles to its
axis. If a fruit be cut into two parts perpendicularly to its axis, the
juice pressed out of each of them, and placed in two cups connected by
a wet strip of paper (*App.* 2), an electric current will be developed in the
same direction; but if the fruit be split in the direction of its axis, the
liquids expressed from the two halves produce no current. The current
is therefore due to the difference of chemical composition between the
juice in the neighbourhood of the stalk, and that at the other end of the
fruit, although both are acid.

b. By Decompositions, effected by the agency of Heat or Light.

Bodies, at the moment of separation from one another, take up the kind of electricity opposite to that which they exhibited during combination.

[According to what has already been said (pp. 328... 330), it must be supposed that when water combines with acids, negative electricity from the water and positive electricity from the acid combine to form heat; and when the water is separated from the acid by evaporation, it must again take up the negative electricity which it has lost, while the acid must recover its positive electricity. This is effected by the decomposition of part of the heat present, the elements of which are divided between the water and the acid. It appears, however, that very small quantities of water and acid get separated from one another without having time to recover their lost electricity. These small quantities of separated aqueous vapour and acid then decompose other portions of heat to make up the deficiency. Thus, the water takes negative electricity, and sets positive electricity free, while the acid takes up positive electricity; so that free negative electricity may be detected in the vessel.

er from alkalis, on the contrary, we might expect
, which the water had lost by its previous
would be again taken up by the aqueous
ld again take up negative electricity, so
et free in the vessel: this, however, is
ecquerel and Fechner (p. 332). It is
ose which are very alkaline, like car-
respect like acids].

ped in the evaporation of pure water, not
a red-hot platinum crucible in which Leiden-
roduced, followed by rapid boiling. (Becquerel;
, 171; Pouillet; Peltier).—Similarly, with the most
sulphuric or nitric acid and glacial acetic acid.—
contains potash, soda, baryta, strontia, or lime in solu-
el constantly becomes positive, feebly during the conti-
Leidenfrost's phenomenon, strongly during the subsequent
With solution of ammonia, the vessel becomes negative, because
case it is principally the ammonia which evaporates, while the
er remains.—If the water contains only $\frac{1}{100}$ sulphuric acid, glacial
cetic acid, or any other acid, or any carbonate, sulphate, chloride, nitrate,
or acetate, the vessel becomes negative. Hence, the electricity of the
atmosphere may in great part be attributed to the evaporation of sea-
water, and other kinds of water not quite pure, on the surface of the earth,
and in the bodies of plants and animals.—When pure water evaporates
in vessels of iron, copper, or silver containing copper, the vessel becomes
negative from commencing oxidation, even when the water contains an
alkali in solution. (Pouillet.)

Peltier remarked that in the evaporation of a solution of common salt, negative electricity was perceptible only at the moment when the remaining salt began to decrepitate,—an effect which also takes place on the decrepitation of crystals of common salt thrown into a red-hot platinum crucible. Hence, according to Peltier, the electricity does not become apparent till the last portions of water separate from the salt.

Vapour escaping from boilers often exhibits positive, and the boiler negative electricity. If one hand, or a plate of metal, or a bundle of wires with numerous points, be held in the stream of vapour, and the other brought near the boiler, a spark may often be obtained from the latter. The higher the pressure, the stronger is the electricity. The cloud of steam which collects under the roof of the building also contains electricity. If the boiler be cleaned from the incrustation, chiefly consisting of gypsum, which lines it, and fed with rain-water, no electricity will be developed: with spring-water, the electricity will not be apparent at first—not in fact till a sediment has been formed; and as this increases, the development of electricity will increase also. (Armstrong.)

By experiments made with a boiler of gun-metal, 30 inches long, 4 inches wide, heated with coke in an insulated furnace, and furnished with a glass tube and stop-cock to regulate the escape of the vapour, the following results were obtained. When the vapour is allowed to escape with the safety-valve open, that is to say, at the ordinary atmospheric pressure, no electricity is apparent; but at 1 lb. pressure per square inch, the electricity begins to show itself. At 3 lb. pressure, the boiler gives a spark after the steam has been escaping for a minute. At 15 lb. pressure,—if the stop-cock be so turned that the quantity of vapour escaping

in a given time shall remain the same,—the quantity of electricity becomes double; at 50 lb. pressure, treble; at 120 lb. quadruple, and at 250 lb. quintuple of what it was at 3 lb. pressure. At 100 lb. pressure a Leyden jar, the knob of which is held in the jet of vapour, while its outer coating is connected with the boiler or furnace, becomes charged in five minutes;—the apparatus may therefore be used as an electrical machine. The vapour is generally positive, the boiler negative. These conditions are seldom reversed; and even when they are, the electricity first becomes apparent at a pressure of 1 lb., and increases, as the pressure rises to 30 lb. in the same ratio as in the former case; but at a still higher pressure, the boiler exhibits negative electricity during the first few minutes of the escape of the vapour, and positive afterwards. When an almost empty boiler is heated till all the water is converted into vapour, the boiler also becomes electrified, on the escape of the vapour, and its electricity is negative. From this it would appear that the development of electricity is due, not so much to the formation of the vapour, as to its precipitation by the cold air (or to its expansion, Gm.?).—The oftener the boiler is used, the more does it become inclined to assume a positive charge; so that at last the vapour almost always exhibits negative electricity. In this case, the inside of the boiler is not found to be oxidated in the slightest degree, and its tendency to become positive is not destroyed by washing it out. But if a very small quantity of potash or soda be added to the water in the boiler (lime does not act so strongly), the vapour once more becomes so strongly positive [*vid.* Pouillet's experiments, p. 337] that it will give thirty sparks, half an inch long, in a minute. A very small quantity of nitric acid or sulphate of copper makes the vapour negative. Hydrochloric acid, sulphuric acid—either alone or mixed with iron filings—and common salt, produce no effect.

¶ Faraday has shown that electricity is never excited by the passage of pure steam, and is manifested only when water is likewise present. Hence he concludes that the effect is altogether due to the friction of the globules against the sides of the opening, or against the substances opposed to its passage, as the water is rapidly moved onwards by the current of steam. Accordingly, it was found to be increased in quantity by increasing the pressure and impelling force of the steam. The immediate effect of this friction was, in all cases, to render the steam positive, and the solids, whatever they might be, negative. In certain circumstances, however, as when a wire is placed in the current of steam at some distance from the orifice, the solid exhibits the positive electricity acquired by the steam, of which it is then merely the recipient and conductor. In like manner, the results may be greatly modified by the shape, nature, and temperature, of the passages through which the steam is forced. Heat, by preventing the condensation of the steam into water, likewise prevents the evolution of electricity, which, however, speedily appears on cooling the passages, so as to restore the water which is necessary for the production of that effect. The phenomenon of the evolution of electricity in these circumstances is dependent also on the *quality* of the fluid in motion, more especially in relation to its conducting power. Water will not excite electricity, unless it be pure: the addition of any soluble salt or acid, even in minute quantity, is sufficient to destroy this property. The addition of oil of turpentine, on the contrary, occasions the development of electricity of the opposite kind to that which is excited *by water;* because each particle of the water becomes covered with a

thin film of oil,—so that the friction takes place only between that external film and the solids along whose surface the globules of liquid are carried. A similar but more permanent effect is produced by the presence of olive-oil, which is not, like oil of turpentine, subject to rapid dissipation. (*Experimental Researches*, Series 18; abstr. *Phil. Mag. J.* 22, 486. —See also Armstrong, *Phil. Mag. J.* 22, 1.) ¶

Pfaff found (*Pogg.* 53, 313) that the vapour issuing from a Papin's digester was positive, and the digester itself negative—even when the water contained potash, carbonate of potash, sulphuric acid, or common salt—the strength of the charge increasing with the tension of the vapour; he also obtained more electricity on holding the metal plate in the vapour at some inches distance from the tube, than when he held it closer.—Williams (*Phil. Mag. J.* 18, 93) also found the boiler negative.

When air is compressed in a metallic vessel to eight times its ordinary density, the vessel generally becomes negative when the stop-cock is opened, and gives sparks a quarter of an inch long, whilst the air which escapes shows positive electricity. More electricity is obtained when the vessel is cold and damp, than when it is warm and dry. A perfectly dry vessel ceases to show signs of electricity even when moderately heated, a damp one not till it is heated strongly; but in the cold, dampness does not seem to increase the electricity. (Armstrong.) [Since the experiment was made with air not perfectly dry, it is possible that water may have been deposited during its compression, and after combining with impurities in the vessel, may have been again converted into vapour on the escape of the air. A repetition of these experiments with dry air is therefore desirable, in order to ascertain whether the electricity proceeds from chemical or mechanical causes.]

If a mixture of water and peroxide of hydrogen be placed in a platinum spoon connected with the galvanometer (*App.* 1), and a piece of spongy platinum, gold, or silver, or even finely-divided ignoble metals, also connected with the galvanometer, be dipped into the liquid,—oxygen gas will be evolved from the peroxide of hydrogen, and positive electricity will pass from the spoon, through the galvanometer, to the spongy metal. If, on the contrary, oxide of silver or hydrate of potash, wrapped up in moist paper and held in the forceps, be dipped into the liquid, an opposite current will be produced. (Becquerel.) [In the first case, oxygen gas is evolved on the surface of the spongy metal,—in the second, on the platinum spoon,—and renders it negative by removing its positive electricity. The water which has lost its oxygen takes up negative electricity, and sets positive electricity free.]

Since, in the combination of carbon with oxygen, the former exhibits negative, the latter positive electricity (p. 329),—it is probable that when carbonic acid is decomposed by plants, under the influence of light, into carbon which is retained by the plants, and oxygen which is set free, the plants will exhibit positive electricity. When seeds are suffered to germinate in mould contained in twelve isolated pans, and the mould in all the pans is connected by a metallic conductor with the condenser of the electrometer, no electricity is perceptible during the first two days of germination; but afterwards, when the plants are more advanced, negative electricity shows itself both in the day-time and at night. In two instances only did the negative electricity gradually diminish, and give place to feeble positive electricity, which continued during the remaining time of the growth. (Pouillet.) [Can the slow combustion of the vegetable mould,

which must have generated negative electricity, have counteracted the regular development of the positive electricity?]—J. Blake (*Phil. Mag. J.* 12, 540) found that—on immersing the leaf of a plant in water, in such a manner that the stalk projected above the liquid, and connecting one end of the galvanometer with the stalk, and the other with the lamina—positive electricity passed from the stalk through the galvanometer into the lamina; the current was stronger in the light than in the dark, but always in the same direction. [This accords with Pouillet's supposition.]

C. *Combinations accompanied by Decompositions.*

α. In Imperfect Conductors.

Electricity in Detonations. In the decomposition of oxalate of silver by heat (whereby it is resolved with a hissing noise into silver and carbonic acid gas) a large quantity of electricity is set free; not, however, when the salt is covered with a watch-glass. Oxalate of suboxide of mercury, oxalate of copper and ammonia, and fulminate of mercury show but little electricity when decomposed by heat. (Dobereiner, *Gill.* 67, 232.)

Fulminate of silver, when exploded by oil of vitriol or by the burning-glass, charges an electrometer on which it is placed, positively. If the decomposition is effected by means of an insulated iron wire heated to redness, positive electricity becomes apparent in a few instances,—more frequently, feeble negative electricity, or none. If the salt is placed in a red-hot platinum spoon, either feeble negative electricity becomes apparent, or none.—Oxalate of silver decomposed by red-hot iron yields positive electricity when it is sifted on a heated platinum spoon. The spoon shows positive electricity if it be strongly ignited, none if heated to faint ignition, negative when still less heated, and none when still colder, but hot enough to decompose the salt with a hissing noise. When oxalate of silver is placed under a watch-glass on the cap of the electrometer, and exploded by a burning-glass, no electricity is developed; but on removing the watch-glass, negative electricity becomes apparent. If the oxalate of silver be exploded on the electrometer by means of a burning-glass, whilst a sheet of tinfoil connected with another electrometer is held at a short distance above it, the first electrometer will show negative, the second positive electricity. Oxalate of suboxide of mercury exploded by a red-hot wire, communicates a strong negative charge to the electrometer.—Oxalate of copper and ammonia, gunpowder, and a mixture of sulphur and chlorate of potash, give no electricity when exploded. (Schweigger.)

By heating certain salts in a platinum crucible connected by a wire with a Bohnenberger's electroscope, till they either explode or decompose with a hissing noise, and removing the spirit-lamp as soon as this decomposition begins, the following results are obtained. Oxalate and citrate of silver give strong, oxalate of copper and ammonia, weak negative electricity. No electricity is manifested by fulminating gold, fulminate of silver, oxalate of suboxide of mercury, and carbazotate of potash, soda, or baryta. (R. Böttger.) Pfaff likewise obtained negative electricity with oxalate and citrate of silver.

Electricity accompanying Decomposition by Simple Affinity. From the first-named substances in the following list, positive electricity goes through the galvanometer to the last-named. From sulphuric acid to nitrate of baryta, and from sulphate of magnesia to potash. (Becquerel.)—From sulphuric, nitric, or hydrochloric acid, to car[illegible]f lime, potash, or

soda; from carbonate of lime to oxalic acid; from sulphuric or nitric acid to chloride of potassium (strong); from sulphuric acid to chloride of barium. (Nobili.)—From oil of vitriol to solutions of common salt, acetate of baryta, or acetate of lead; from concentrated solution of sulphate of alumina or blue vitriol, to ammonia; from nitrate of silver to hydrochloric ; from perchloride of iron to concentrated or dilute sulphuric acid, ammonia, or potash. (Walcker.)—For complicated cases with *App.* 10, *vid.* Fechner (*Pogg.* 48. 1 and 225).—In the decomposition of calomel by nitric acid, positive electricity goes from the acid through the galvanometer to the calomel. (De la Rive.)—When carbonate of potash is decomposed by dilute sulphuric acid in a metallic vessel standing on the electrometer, the instrument shows a negative charge. (Lavoisier & Laplace, *Crell, Ann.* 1788, 1, 351). [I have also obtained negative electricity].

Electricity in decompositions by Double Affinity. Positive electricity goes from green vitriol through the galvanometer to ferrocyanide of potassium; from tincture of galls to green vitriol. (Becquerel.)—From alkaline sulphates to nitrate of baryta. (Nobili.)—From chloride of barium to carbonate of soda; from chloride of calcium to sulphate of copper; from perchloride of iron to hydrosulphuret of ammonium or ferrocyanide of potassium; from sulphuret of copper to carbonate of soda or ferrocyanide of potassium; from nitrate of silver to common salt, acetate of potash, or ferrocyanide of potassium; from chloride of gold or platinum to ferrocyanide of potassium. (Walcker.)—For complicated cases with four vessels, *vid.* Fechner.

Electricity in Fermentation. If two horizontal metal plates connected with the galvanometer be immersed in fermenting beer-wort, one at the bottom of the vessel, the other near the surface of the liquid, positive electricity proceeds, at first—so long as the yeast remains at the bottom—from the lower plate through the galvanometer, to the upper; afterwards when the yeast rises to the surface, the current takes the opposite direction. Hence it appears that negative electricity always proceeds from the yeast (on which the bubbles of carbonic acid gas are evolved.)—*J. Blake* (*Phil. Mag. J.* 12, 539.)

β. *In the Action of Perfect on Imperfect Conductors.*

Simple Galvanic Circuit.

1. *Two Metals and one Liquid.*

When two metals are placed in contact with an imperfectly conducting compound liquid, and connected together at some point within or without the liquid, either immediately or by means of a good conductor (a wire),—and moreover, one of these metals has the power of decomposing the liquid by appropriating one or more of its elements, whilst the other is either destitute of this power or possesses it only in a less degree,—then (1). Decomposition takes place, and a new compound is formed on the first metal only; whereas the second, if placed alone in the liquid, would in many cases exert a decomposing action upon it, and deprive it of the very elements which are actually taken from it by the first metal; (2). The decomposition goes on more quickly than it would, if the first metal were placed alone in the liquid. (3). Those elements of the liquid which are set free by the abstraction of the others, do not make their appearance at the surface of the first metal, where the action takes place, but at the surface of the second. (4). This action is invariably accompanied by a powerful electric current; and, when the first metal takes from the liquid,

oxygen, chlorine, iodine, sulphur, and the other so-called electro-negative substances—and liberates hydrogen, metals, and other so-called electro-positive substances,—positive electricity goes directly from the passive to the active metal, and—if the current be supposed to continue through the liquid—from the acting metal through the liquid to the passive metal.

[*a*. The so-called electro-negative bodies, viz. oxygen, chlorine, bromine, sulphur, &c. contain positive electricity as well as heat in the combined state, and the so-called electro-positive bodies, as hydrogen and metals, contain negative electricity similarly combined. In the combination of an electro-positive with an electro-negative body, the opposite electricities neutralize one another more or less completely and produce fire; in water, *e. g.* the oxygen has lost its positive, and the hydrogen its negative electricity (p. 157, 158).

b. When a metal, such as zinc, comes in contact with water, its great affinity for oxygen causes the oxygen-atoms of the contiguous atoms of water to turn towards the zinc, and the hydrogen-atoms the contrary way. This arrangement is propagated throughout the whole mass of water, so that the hydrogen-atom of each atom of water is turned towards the oxygen-atom of the next. (*App.* 12.)

c. The oxygen-atoms lying nearest to the zinc unite with it and form oxide of zinc. This sets free the negative electricity of the zinc. At the same time, the nascent hydrogen has to recover the negative electricity which it had lost by combination with oxygen in the form of water: it therefore takes this negative electricity from the zinc. But the oxygen-atom situated between the zinc and the hydrogen-atom interferes with this transference of electricity: consequently, an extremely small quantity of negative electricity becomes accumulated in the zinc, and a corresponding quantity of positive electricity in the water; because that portion of the nascent hydrogen which does not receive negative electricity from the zinc takes it from the caloric of the water, and therefore sets free some of the positive electricity of that liquid.

d. When another metal, copper for example, is placed in the water near the zinc, but without touching it, this metal likewise attracts the oxygen-atoms of the water,—and we may suppose that, since the atoms of water turn their oxygen-atoms towards both metals, a limit x will be found between the two metals, but nearer to the copper than to the zinc, at which every two hydrogen-atoms come in contact with each other.

e. If, on the other hand, zinc and copper—or another metal whose affinity for oxygen is less than that of zinc—are placed in metallic contact, either directly or by means of a wire (*e. g.* that of the galvanometer), the following change takes place. The negative electricity set free in the zinc passes over, in greater or less quantity, directly to the copper;—thence it attracts the hydrogen-atom of the adjacent atom of water in every series of atoms of water situated between the zinc and copper,—passes over to it, and causes it to escape in the form of hydrogen gas. In this case, all the oxygen-atoms are turned towards the zinc, and all the hydrogen-atoms towards the copper, in consequence of the attraction exerted upon them by the negative electricity issuing from that metal. *It is immaterial whether we say that negative electricity goes through the metallic arc from the zinc to the copper, or positive electricity from the copper to the zinc.*

f. In each series of atoms of water between the zinc and copper, a mutual displacement of the oxygen-atoms from the copper towards the zinc, and of the hydrogen-atoms from the zinc towards the copper, must be

supposed to take place,—the water remaining unaltered in composition throughout its whole mass; while the fixation of oxygen takes place only at the surface of the zinc, and the liberation of hydrogen at the surface of the copper. Suppose, for the sake of illustration, that only four atoms of water are situated in a row between the zinc and copper (the actual number, even with a small interval between the metals, would probably be several millions):—then, the zinc takes up the oxygen-atom 1, and the hydrogen-atom 4 escapes at the surface of the copper. Next, the hydrogen-atom 1 unites with the oxygen-atom 2; and similarly, H 2 with O 3, and H 3 with O 4,—and, notwithstanding the separation of the two elements of the water in different places, every thing in the middle remains apparently tranquil and unaltered, and no visible current is formed in the water. (*App.* 15, *a.*) Since now one atom of water has disappeared from the series, another atom, 5, is transferred to the series from the surrounding water. (*App.* 15, *b.*) In this series, all the hydrogen-atoms are turned towards the zinc; but the affinity of that metal for oxygen immediately causes the atoms of water to turn half round, so that all the oxygen-atoms may be directed towards the zinc. (*App.* 15, *c.*) The zinc then combines with O 2, and H 5 is evolved at the surface of the copper; and thus the process is repeated, as long as the oxidation of the zinc goes on. The hydrogen-atoms move in semi-circles towards the right, first upwards and then downwards,—the oxygen-atoms towards the left alternately upwards and downwards, till the former reach the surface of the copper and there escape, the latter, the surface of the zinc and combine with that metal. This simultaneous transposition of the two kinds of atoms may be represented by the lines in *App.* 16.

g. It appears then that there are two kinds of chemical action to be distinguished: the *purely-chemical* and the *electro-chemical.* The former takes place when zinc is placed alone in contact with water (*b, c,*): it does not give rise to an electric current, because the negative electricity passes directly from the zinc to the hydrogen. But when the zinc is connected with another perfect conductor—which in this case plays only the passive part of transferring the negative electricity to the hydrogen (*e, f,*)—electro-chemical action is produced, the electricity passing along from the zinc to the copper—even when the connecting wire is of great length—and giving rise to a mutual transposition of the atoms.

h. The cause of both pure chemical and electro-chemical action is to be found in the affinity of zinc for oxygen; that of the latter, more especially, in the obstacle which the oxygen-atom situated between the zinc and the hydrogen-atom opposes to the transference of negative electricity from the zinc to the hydrogen. For, the electricity being able to traverse metals with the greatest facility and rapidity, prefers the circuitous road from the zinc to the copper, and transposes the atoms of the water, which —since it possesses the peculiar mobility of a liquid, and since the new compounds formed are equal in number to the atoms decomposed—appears to offer no great opposition to the change.

i. This last-mentioned opposition is, however, in most cases sufficiently great to cause a part of the purely chemical action to go on simultaneously with the electro-chemical. The negative electricity avails itself of both paths to pass from the zinc to the hydrogen—the direct route and that through the copper. The stronger the purely chemical action, the weaker is the electric current. The electro-chemical action, and therefore the electric current, is strengthened, and the purely chemical action proportionally weakened: 1. By diminishing the distance between

the copper and zinc within the liquid,—because the difficulty caused by the transposition of the atoms is thereby somewhat lessened.—2. By increasing the surface of copper in contact with the liquid,—because the transference of the negative electricity from the copper to the hydrogen of the water is thereby facilitated.—3. By facilitating the mechanical removal of the bubbles of hydrogen which accumulate on the copper and diminish its acting surface.—4. By purifying the zinc, and consequently equalizing the power with which the different points of its surface attract the oxygen of the water. For even if the zinc contains but a small quantity of other metals (except mercury), these impurities, in combination with a small portion of the zinc, form alloys, which, being mechanically diffused through the rest of the metal, and having less affinity for oxygen than pure zinc, produce an action similar to that of copper—that is to say, while the oxygen goes over to the pure zinc, these alloys transfer the liberated negative electricity to the hydrogen, thereby producing a *local electro-chemical action*, by which the current from the zinc to the copper is weakened.—5. An opposite effect is produced by covering the surface of the zinc with mercury. Amalgamated zinc exhibits with water and dilute acids, only electro-chemical, not purely chemical action. What it is that here prevents the direct passage of the negative electricity from the zinc to the hydrogen remains yet to be discovered.—6. The nature of the liquid has likewise some influence. Thus, water is more inclined to electro-chemical, nitric acid to purely chemical action—possibly, because the oxygen-atom offers a more effectual obstacle to the transference of electricity from the zinc to the minute atoms of hydrogen, than to the much larger atoms of nitric oxide evolved from the nitric acid,—which indeed, from their greater size, must project beyond the atoms of oxygen.

k. Zinc connected with copper takes up the oxygen of a watery liquid more easily and quickly than zinc alone,—and consequently liberates a greater quantity of hydrogen gas in a given time: for the points of transference of negative electricity to hydrogen are multiplied, and the transference thereby facilitated.

l. Since, in the action of water upon zinc, the oxide, as it forms, is deposited on the surface of the metal, and thereby offers a continually increasing obstacle to its contact with the water, the oxidation proceeds very slowly, both when the zinc is alone, and when it is connected with copper:—hence, even in the latter case, the quantity of negative electricity which passes over in a given time is but small. The presence of an acid and certain other substances accelerates the oxidation of the zinc—1. By the predisposing affinity of the acid for the oxide of zinc produced,—and 2. By dissolving the oxide and keeping the surface of the zinc clean. By this addition, the quantity of negative electricity which passes over in a given time from the zinc to the copper is much increased —in other words, a current of much greater *Quantity* is produced; but the *Intensity* of the current,—that is to say, its velocity and power of overcoming the obstacles which interfere with its motion—is not on that account necessarily increased: for the intensity depends on the quantity of negative electricity which can accumulate in zinc unconnected with copper, before it acquires a sufficient force to overcome the obstacle presented by the oxygen-atom between the zinc and hydrogen-atom, and pass directly to the hydrogen. It may likewise be supposed that the atom of zinc-salt formed when an acid is present, moves onward, together with the adjacent hydrogen-atom, from the zinc towards the copper in the manner described in *f*,—whilst the free acid, in connection with the

oxygen-atoms of the water, is transferred from the copper towards the zinc side.

m. Similar actions take place when zinc and copper are immersed in other liquids. From nitric acid zinc takes oxygen, while negative electricity passes over to the liberated nitric oxide gas. From sulphuret of potassium, containing several atoms of sulphur, zinc takes sulphur,—and negative electricity passes over to the sulphuret of potassium, which has thus been deprived of part of its sulphur: and so on.

n. The rest of the metals and other perfect conductors exhibit relations similar to those of zinc and copper, at least when one of the two conducting bodies immersed in a liquid is capable of decomposing it. The direction of the current is always determined by the difference of affinity of the two conductors for the electro-negative element of the liquid. Negative electricity always proceeds from the metal, which by its greater affinity appropriates the electro-negative element, through the connecting wire to the other metal,—or, what comes to the same thing—positive electricity goes from the latter metal to that which is in the act of combination, and possibly, from this through the liquid to the inactive metal. The *quantity* of the electric current is directly proportional to the strength of the electro-chemical action. The greater the quantity of the electro-negative element taken up by the metal, the greater also will be the quantity of electricity which passes over,—provided always that no purely chemical action take place at the same time,—for the effect of this would be to weaken or arrest the electric current. The following circumstances accelerate the combination of the metal with the electro-negative element of the liquid, and may therefore increase the electric current: Increase of affinity and diminution of cohesion in the metal,—rise of temperature,—increased facility of conveying the negative electricity from the electro-negative metal to the liquid, depending upon cleanliness and extent of surface.—The *tension* or *intensity* of the electric current is perhaps greater in proportion to the difference between the affinities of the two metals for the electro-negative element; the influence of the circumstances noticed in *i*, 1, must however be taken into account.

o. The metal endowed with the greater affinity for the electro-negative element of the liquid may, by its action, become covered with a product which may interrupt wholly or partially the contact between the liquid and the metal; in such a case, the affinity of the other metal may come into play, and give rise to a *reversal of the current.*

p. Two perfect conductors may produce a current, even without abstracting any element of the liquid, provided one of them give up one of its own elements to the liquid or the metal. Thus, from peroxide of manganese, lead, or silver, immersed in different liquids, positive electricity passes over through the galvanometer to platinum or copper. For, when a body of this nature gives up oxygen to the liquid, or transmits it by displacement of particles to the metal, the oxide, being more or less reduced, recovers its lost negative electricity by appropriating that which flows to it through the connecting wire from the platinum or the copper,—the metal either receiving this negative electricity from the liquid which gives it up on combining with the oxygen, or evolving it directly, when it takes up the oxygen itself.]

Experiments with Water. On placing one above the other, brass, zinc, dry wood, damp wood, zinc, and brass, the last-mentioned brass imparted negative electricity to the condenser of the electrometer. (De la Rive.)—

The same result was obtained with copper, zinc, four sheets of dry paper, one sheet of damp paper, zinc, copper;—the two copper-plates may also be omitted;—the first zinc gave positive, the second negative electricity to the electrometer. Again, when a bar of zinc is wrapped round with paper and one-half of the paper wetted, the wet end imparts positive electricity to the electrometer; the dry end—if a damp sheet of paper be laid on the condenser to facilitate the conduction—negative electricity. (Fechner.) [Negative electricity accumulates in the last zinc (p. 342, *c*), positive electricity in the damp wood or paper; and these are communicated to the electrometer, when it is brought in contact with the zinc or the moisture.]

A solution of 1 part of potassium in 100 parts of mercury is, when placed in water, strongly positive towards platinum; polished lead is also positive towards platinum. Potassium being soluble in water, and oxide of lead likewise soluble though in a slighter degree, these substances can produce a strong current without the intervention of an acid. (Faraday*.)

If a strip of zinc and a strip of platinum in water deprived of air give at the commencement of the action a deflection of 15°, this deflection will be reduced to 1°, when the circuit has been closed for some time; but will again rise to 15°, after the circuit has been left open for 24 hours. Zinc which has become inactive by immersion, together with platinum, in water free from air, is negative towards zinc freshly immersed. In water containing air, on the contrary, a pair of zinc and copper gives a constant deflection of 15°. (Buff.)

Iron, which rusts when placed by itself under water, remains bright when in contact with zinc, the latter alone becoming oxidated. (Wetzlar.) —The so-called *Galvanized Iron* is iron protected *by a coating* of pulverized zinc.

Polished lead is positive towards iron in pure water, tarnished lead negative. (Yorke.)—In pure water, lead is constantly, but very feebly, positive towards iron,—the iron likewise oxidating, though in a less degree. In spring-water, the lead is positive at first; but the iron soon becomes positive, remains so, and oxidates. (Wetzlar.) [Perhaps a deposit forms on the surface of the lead (p. 345, *o*).]

Gold and platinum together produce no current in pure water (Walcker, Becquerel); neither does gold or platinum produce a current with magnetic iron ore, specular iron, red oxide of copper, or iron pyrites (Becquerel.)

If the wet and dry ends of a piece of peroxide of manganese be connected with the galvanometer, positive electricity passes from the dry end through the galvanometer to the wet end. A crystal of peroxide of manganese is feebly positive towards platinum in water, as shown by the galvanometer; the current soon ceases, but reappears if the circuit be left open for not less than five minutes. Platinum exhibits similar relations with graphite or anthracite, excepting that the latter becomes positive.—

* These and most of the following experiments were so arranged that the metals in contact with the liquid were connected with the ends of the galvanometer. When it is said, in accordance with the received phraseology, that one metal is positive with regard to another, and the latter negative with regard to the former, it is to be understood that positive electricity goes from the negative metal through the galvanometer to the positive metal (and, as is sometimes assumed, from the positive metal through the liquid to the negative metal). In short, the positive metal is that which is chemically active—and, by taking up the electro-negative element of the liquid, developes negative electricity within itself, and sends it through the galvanometer to the inactive, negative metal,—or receives positive electricity from the latter (p. 342, *c*).

Likewise gold, magnetic iron ore, specular iron, red oxide of copper, and iron pyrites, become positive in water with peroxide of manganese or graphite. (Becquerel.) [With respect to peroxide of manganese, *vid.* p. 345, *p.*—Does the action of graphite result from its having absorbed oxygen from the air?] Platinum is positive towards peroxide of lead in pure water. (Schönbein.)

If platinum be laid on the condenser of the electrometer, damp paper on the platinum, peroxide of manganese on the paper, and the oxide of manganese touched with dry wood, the condenser will show positive electricity. When platinum and peroxide of manganese are connected with the galvanometer, positive electricity passes from the peroxide of manganese through the galvanometer to the platinum. In pure water, the current is very weak,—but stronger with irregularly crystallized peroxide of manganese than with large single crystals, because the former is more prone to decomposition. If the oxide of manganese be left for a considerable time in water by itself, and then connected with platinum in nitric acid, the current at first goes the contrary way—a proof that the oxide of manganese has been superficially altered by the water. (De la Rive.)

If zinc with copper and water give an indication of 4° in the voltaic electrometer, it will give $4\frac{1}{2}$ with silver, $4\frac{3}{4}$ with charcoal, 5 with gold, $5\frac{1}{2}$ with black sulphuret of mercury, 6 with iron pyrites, $6\frac{1}{2}$ with peroxide of manganese, and $9\frac{1}{2}$ with peroxide of lead. (Rosenchöld.)

Electrical series of metals in water, beginning with the most highly electro-positive: Zinc, lead, tin, iron, antimony, bismuth, copper, silver, gold. (Fechner.)

Experiments with Dilute Acids, not including Nitric Acid.—A solution of 1 part of potassium in 1000 parts of mercury is highly positive towards zinc.—Amalgam of zinc is positive towards zinc, and amalgam of tin towards tin. (H. Davy.)

Perfectly pure zinc dissolves more slowly in dilute sulphuric acid than commercial zinc, which contains 1 per cent. of iron, together with cadmium and traces of lead and tin—or than an alloy of 10 parts of zinc with 1 part of tin, lead, iron, or copper,—because these impurities give rise to local electro-chemical action (p. 344, *i.* 4). When commercial zinc and pure zinc are placed in dilute sulphuric acid of various degrees of strength (the annexed per centages show the quantities of anhydrous sulphuric acid in the liquid), the times required to furnish a given quantity of hydrogen gas are found to be as follows:

	20·2	25·64	29·85	35·28	43·25	64·2	per cent.
Commercial zinc ..	3	1·5	1	1·5	2	4·5	
Pure zinc	108	55	15	13	12	45	

Hence, commercial zinc is most quickly dissolved by dilute sulphuric acid containing from 25 to 43 per cent. of real acid,—and pure zinc by that which contains from 30 to 43 per cent. The evolution of gas is very slow at first, but gradually increases, reaching its maximum in 10 minutes with commercial zinc, and after several hours with pure zinc: with acid of 64 per cent, however, the evolution of gas soon diminishes. [Does this arise from the formation of a film of sulphate of zinc?] *De la Rive.*

Alloys of 10 parts of zinc, with 1 part of tin, lead, iron, or copper, being immersed in dilute sulphuric acid of various degrees of strength, a comparison of the times required for the evolution of a given quantity of hydrogen gas, with the corresponding intervals in the case of pure and commercial zinc, gives the following results:

	20·2	25·64	29·85 p. c.
Pure zinc	207	110	30
Commercial zinc	4	3	2
Tin-zinc	24	12	12
Lead-zinc	12	9	10
Iron-zinc	4	3	2
Copper-zinc ..	5	6	4

With copper-zinc the evolution of gas continually diminishes, because the alloy becomes covered with a black film of oxide of copper [metallic copper?]; when this is removed, the evolution of gas again becomes rapid. —The solution of pure zinc is greatly accelerated by binding it round with platinum wire. (De la Rive.)

When four balls of zinc of equal size are immersed for an hour in equal quantities of dilute sulphuric acid, contained in four vessels of equal size, but different materials, the quantity of zinc dissolved in the glass vessel is found to be 1·5, in the silver vessel 51, in the gold vessel 65, and in the platinum vessel 79 millegrammes. On being afterwards immersed for an hour in four glass vessels containing equal quantities of acid of the same strength, the ball previously immersed in the other glass vessel loses 1·5, that from the silver vessel 5, from the gold 8, and from the platinum 11 millegrammes. (Bouchardat, *Ann. Chim. Phys.* 53, 284.) [Had the balls the same temperature in the second experiment?]

Balls of zinc immersed for the same time in dilute sulphuric acid, dilute hydrochloric acid, or solution of ammonia, lose, according to Bouchardat, the following quantities, varying with the nature of the containing vessel.

Vessels.	Hyd. ac.	Sulph. ac.	Am.
Glass	4	3	
Sulphur	5	3	1
Black lead ..	10		
Tin	12	12	12
Lead	14	28	15
Antimony ..	41	38	18
Bismuth	45	38	20
Silver	58	65	22
Gold	52	100	24
Platinum.....	55	116	27
Copper	70	150	40
Brass	124	190	103
Iron		130	

With balls of commercial zinc, the loss of weight in dilute sulphuric acid in a quarter of an hour amounts, in glass vessels to 9, in sulphur to 10, in lead to 310, in antimony to 350, in bismuth to 342, in silver to 665, and in platinum to 712. (Bouchardat.)

Two zinc plates of equal size being placed in dilute sulphuric acid (1 part oil of vitriol with from 8 to 16 of water), and one of them connected with a plate of polished lead, the second loses much less weight than the first (this is contrary to Bouchardat's statement); with hydrochloric acid an opposite result is obtained. (Runge, *Pogg.* 43, 581.)

To obtain amalgamated zinc, mercury is placed upon the zinc, together with dilute sulphuric acid, and both liquids spread upon the plate by means of a pad of cloth or linen, the acid being from time to time renewed. (Masson, *Ann. Chim. Phys.* 60, 334.) Or the bottom of a capacious dish being covered with mercury and sulphuric acid poured upon it, the zinc plate is immersed in the acid, its surface touching the mercury,—turned after two or three hours, and afterwards taken out. (Liebig, *Ann. Pharm.* 29, 111.) [This covering of the zinc with mercury depends on a peculiar galvanic action. The mercury,—which is in contact with the zinc at one point, and takes up the negative electricity set free in the zinc,—instead of giving rise to a transposition of atoms in the water, attaches itself, in consequence of its mobility, to the zinc, and thus imparts negative elec-

tricity directly to the hydrogen-atom of the atom of water which has given up its oxygen to the zinc.]

Amalgamated zinc when alone is not attached by dilute sulphuric acid; but when it is connected with platinum or other metals, a powerful action takes place, the hydrogen gas being wholly evolved on the surface of the platinum, not upon the zinc. (Faraday.)—Amalgamated zinc immersed in dilute sulphuric acid becomes covered after a time with gas-bubbles, which adhere strongly to it; no loss of weight can be detected in the zinc, even after four-and-twenty hours. The adhering hydrogen gas appears then to protect the zinc from the action of the liquid. When amalgamated zinc is connected with platinum, the hydrogen being all transferred to the platinum, the zinc is dissolved. If the dilute sulphuric acid contains a little nitric acid mixed with it, that acid converts the hydrogen into ammonia, and then the amalgamated zinc dissolves, even though not connected with platinum. (Daniell, De la Rive.) [But pure zinc likewise becomes covered with bubbles, and dissolves nevertheless.]—The coating of mercury makes the surface of the zinc uniform, so that the alloys possibly contained in it cannot give rise to any local electro-chemical action; it therefore makes commercial zinc like pure zinc. (Grove.) [But pure zinc dissolves, although the action goes on slowly,—amalgamated zinc not at all.] The mercury appears to prevent, in some unknown manner, the direct transference of negative electricity from the zinc to the hydrogen (p. 345, *i*, 5.)

Amalgamated zinc in dilute sulphuric acid is positive towards the same metal unamalgamated (H. Davy); because the latter, in consequence of the strong purely chemical action, is more quickly surrounded with saturated sulphuric acid [which, however, should be soonest removed by the rapid disengagement of gas]. (Faraday.)

When two pieces of amalgamated zinc of the same size are immersed in dilute sulphuric acid, and one of them is connected with copper, the latter piece loses 32·31 parts for every 1 part of hydrogen evolved at the surface of the copper (1 at. H. to 1 at. Zn.), while the other piece suffers no diminution. (Faraday.)

Amalgamated zinc produces with copper a much more copious current than ordinary zinc. (Poggendorff.)

An amalgamated zinc plate, connected with copper, and immersed in dilute sulphuric acid, loses more weight in the second half hour than in the first, in the third more than in the second, and so on, till it is again amalgamated. (Binks.)

Amalgamated zinc in dilute sulphuric acid, in connection with amalgamated copper which dips into mercury, or only with amalgamated platinum, is at first strongly positive,—but the current ceases in a few minutes: but on replacing the amalgamated zinc by unamalgamated platinum, a current in the contrary direction is set up. The amalgamated metal is positive. The mercury probably combines with hydrogen, and thereby becomes as strongly positive as the amalgamated zinc. (Grove.)

Black lead or freshly ignited gas-coke placed in sulphuric acid with amalgamated zinc immediately liberates hydrogen gas; porous coke and box-wood charcoal, on the contrary, not till after some time, because they absorb the first portions of liberated hydrogen. If they are then placed by themselves in a solution of lead, copper, mercury, silver, or gold, they become covered with a thin metallic film, just as they liberate iodine from iodic acid. Coke retains hydrogen for forty-eight hours. (Smee.)

Zinc gives with iron in dilute sulphuric acid a current four times as

ric acid, on the contrary, the solution of iron is accelerated by contact both lead. (Runge.)

In cold dilute sulphuric acid, tin is feebly positive towards lead; slightly negative, when the acid is warm. Towards iron, tin is positive in cold acid, often slightly negative in warm acid. (Faraday.)

Antimony in dilute sulphuric acid is positive towards bismuth. (Fechner.)

Iron in dilute acid is strongly positive towards arsenic. (De la Rive.)

Nickel in dilute sulphuric acid is positive towards antimony and bismuth. (De la Rive.)

Copper in dilute acids is positive towards silver and platinum; so also is silver towards platinum. (Walcker.)

Gold exerts a scarcely perceptible positive reaction towards platinum in dilute sulphuric acid. (Ritchie.) In dilute sulphuric acid it is positive; in dilute hydrochloric acid, negative. (Walcker.)—In a mixture of 1 part oil of vitriol and 100 water, it is at first positive,—then, after several immersions, neutral, and subsequently negative. (Marianini.)

Palladium gives no current with platinum in pure hydrochloric acid, but becomes positive on the addition of nitric acid. (De la Rive.)

Anthracite in dilute sulphuric or hydrochloric acid is negative towards copper, silver, or platinum. (Becquerel.)

Platinum is at first positive towards graphite, neutral after several immersions, then negative. The graphite remains unaltered; but the platinum is rendered positive towards other platinum, losing this property, however, by ignition or immersion in boiling water. Gold and silver exhibit similar relations towards graphite, but in a lower degree. When platinum, gold, or silver is immersed in contact with graphite till it ceases to produce deflection of the needle, and then,—while still remaining in the acid—connected for a short time with zinc, it again becomes positive to graphite. Possibly, when these metals are placed in contact with graphite, a portion of oxygen becomes fixed upon them, and renders them more negative; and when they are connected with zinc, this oxygen is removed by the hydrogen, the latter then accumulating on the surface of the metal: for platinum which has been in contact with zinc under dilute acid is positive towards platinum which has not been so treated. (Marianini.)

Platinum is feebly positive towards peroxide of manganese in dilute acid. (De la Rive).

Pairs of plates of the same size of different metals immersed in very dilute sulphuric acid produce the following deflections of the needle:

Zinc with lead 9·0°, with iron 6·3°, with copper 8·0°, with gold 6·0°, with platinum 3·3°.—*Tin* with copper 5·0°, with silver 4·0°, with gold or platinum 1·0°.—*Lead* with iron 2·0°, with copper 5·3°, with silver 4·3°, with gold 1·5°, with platinum 2·0°.—*Iron* with copper 3·0°, with gold or platinum 1·0°.—*Copper* with silver 3·3°, with gold or platinum 0·3°.—*Silver* with gold or platinum 0·3°. The positive metal in each case has its name printed in *italics*.—These deflections are not in accordance with the theory of contact. The smallest deflections are those obtained with pairs containing gold or platinum;—it is true that platinum does not conduct so well as silver; but gold conducts better—and yet copper and silver give a stronger deflection than copper and gold. (Marianini.)

Electrical series of perfect conductors in dilute acids,—each body of the series being negative with those which precede, and positive with those which follow it:

abundant as with copper, the size of the plates being the same in both cases,—so that a ten-pair battery of zinc and iron yields in seven minutes (if the polar wires are made to dip into water) as much detonating gas as a battery of zinc and copper of the same dimensions. But it is only the quantity of the electric current that is greater in the case of zinc and iron; the tension is smaller. At the first moment of immersion, the quantity also is greater with zinc and copper; but the copper soon becomes covered with a dark film of oxide [sulphuret?], while the iron remains clean,—and this film interferes with the electrical conduction between the copper and the liquid. When a pair of zinc and iron plates, and a pair of zinc and copper, are left in action for twelve hours, the following loss of metal is observed: Copper, 0; zinc connected with it, 96 grains; iron, 6 grains; zinc connected with it, 74 grains. It appears, then, that a small quantity of iron is dissolved; and of the zinc connected with copper more than of the other zinc,—and yet the quantity of the current is greater with zinc and iron. [Hence, zinc and copper produce a greater amount of purely chemical action]. (Martyn Roberts, *Phil. Mag. J.* 16, 142; 19, 106.)

Zinc and iron produce a more copious current than even zinc and silver or zinc and platinum, both in dilute sulphuric and dilute nitric acid; and the plates of the zinc and platinum pair must have a surface three times as great as that of the zinc and iron to yield the same quantity of electricity. But the intensity of the current excited by zinc and iron is smaller. If the quantity of electricity yielded by zinc and iron be 260, that yielded by zinc and copper is 100: when the plates are connected by a wire 50 feet long, the quantity yielded by zinc and iron is 33·7, and by zinc and copper 18. The resistance of the long wires diminishes, therefore, the quantity yielded by zinc and iron from 100 to 13, and by zinc and copper, from 100 to 18.—When the plates are connected by a fine wire 2000 feet long, the quantity of electricity yielded by zinc and iron is to that furnished by the zinc and copper as 1000 : 1678. With amalgamated iron, zinc yields a much feebler current than with common iron. (Poggendorff.)

Göttling (*Gilb.* 28, 475) constructed a powerful pile with plates of iron covered with zinc on one side, and moistened pieces of cloth.

Cadmium is positive towards iron in dilute sulphuric acid, and yields 400 times more electricity than copper with platinum. Nevertheless, more iron than cadmium is dissolved. (Poggendorff.) [This deserves attention.]

Tin is positive with lead in concentrated aqueous solution of oxalic or tartaric acid, negative in very dilute solutions. (Fechner.)—Tin is positive with iron or copper in dilute acid (De la Rive); and a steel wire consequently remains bright, and loses no weight, when placed in contact with tin under dilute hydrochloric acid. (J. Davy.)

The following are the weights lost by tin balls of equal size placed for an hour in very dilute hydrochloric acid, contained in vessels of different materials: in vessels of glass or sulphur, 3; of lead, 12; silver, 19; antimony, 34; bismuth, 36; copper, 70; platinum, 85; gold, 201. (Bouchardat.)

Polished lead is positive in dilute acid towards iron and copper, tarnished lead negative. (Yorke.) In dilute hydrochloric or sulphuric acid, iron is, after the first moment, positive towards lead. (Wetzlar.) [Was the lead quite clean?].—Iron, when in contact with lead, dissolves more *slowly in dilute* sulphuric acid than when alone: after a few days, the *iron becomes dull,* and covered with sulphate of lead. In dilute hydro-

loric acid, on the contrary, the solution of iron is accelerated by contact with lead. (Runge.)

In cold dilute sulphuric acid, tin is feebly positive towards lead; slightly negative, when the acid is warm. Towards iron, tin is positive in cold acid, often slightly negative in warm acid. (Faraday.)

Antimony in dilute sulphuric acid is positive towards bismuth. (Fechner.)

Iron in dilute acid is strongly positive towards arsenic. (De la Rive.)

Nickel in dilute sulphuric acid is positive towards antimony and bismuth. (De la Rive.)

Copper in dilute acids is positive towards silver and platinum; so also is silver towards platinum. (Walcker.)

Gold exerts a scarcely perceptible positive reaction towards platinum in dilute sulphuric acid. (Ritchie.) In dilute sulphuric acid it is positive; in dilute hydrochloric acid, negative. (Walcker.)—In a mixture of 1 part oil of vitriol and 100 water, it is at first positive,—then, after several immersions, neutral, and subsequently negative. (Marianini.)

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Platinum is at first positive towards graphite, neutral after several immersions, then negative. The graphite remains unaltered; but the platinum is rendered positive towards other platinum, losing this property, however, by ignition or immersion in boiling water. Gold and silver exhibit similar relations towards graphite, but in a lower degree. When platinum, gold, or silver is immersed in contact with graphite till it ceases to produce deflection of the needle, and then,—while still remaining in the acid—connected for a short time with zinc, it again becomes positive to graphite. Possibly, when these metals are placed in contact with graphite, a portion of oxygen becomes fixed upon them, and renders them more negative; and when they are connected with zinc, this oxygen is removed by the hydrogen, the latter then accumulating on the surface of the metal: for platinum which has been in contact with zinc under dilute acid is positive towards platinum which has not been so treated. (Marianini.)

Platinum is feebly positive towards peroxide of manganese in dilute acid. (De la Rive).

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Electrical series of perfect conductors in dilute acids,—each body of the series being negative with those which precede, and positive with those which follow it:

According to Sir H. Davy: Potassium and its amalgam, barium and its amalgam, zinc-amalgam, zinc, ammonium-amalgam, cadmium, tin, iron, bismuth, antimony, lead, copper, silver, palladium, tellurium, gold, platinum, iridium, rhodium. Rolled copper is positive towards that which contains carbon (overpoled); this towards the same metal containing suboxide (underpoled); and this towards copper containing tin.

According to Faraday: In a mixture of one measure of oil of vitriol with one measure of water: Zinc, cadmium, tin, lead, iron, nickel, bismuth, antimony, copper, silver.

According to Pfaff: Zinc, cadmium, tin, lead, tungsten, iron, bismuth, antimony, copper, silver, gold, tellurium, platinum, palladium.

According to Marianini,—in very dilute sulphuric acid: Zinc, charcoal immediately after being cooled in water (containing hydrogen therefore) polished lead, tin, manganese, tarnished lead, iron, magnetic iron ore, brass, copper, brass very much corroded, bismuth, nickel, charcoal soon after being quenched in water, bright antimony, tinstone, native sulphuret of molybdenum, bright arsenic, tarnished antimony, silver, mercury, tarnished arsenic and arsenical silver, red silver, galena, freshly prepared charcoal, copper-nickel, copper-glance, arsenical cobalt, black tellurium, copper pyrites, platinum, gold, auriferous native tellurium, cubical iron pyrites, graphite, arsenical pyrites, magnetic pyrites, amorphous iron pyrites, peroxide of manganese, charcoal long exposed to the air.

Experiments with Concentrated Hydrochloric Acid. Zinc gives with platinum a current which is feeble as long as the chemical action continues powerful, but becomes stronger as the chemical action diminishes. (Pfaff.)

Tin is negative with lead at the beginning of the action, but afterwards becomes permanently positive, because the lead acquires a coating of chloride of lead.—Nickel is positive towards antimony and negative to bismuth. (Faraday.)

In fuming hydrochloric acid, bismuth and copper are positive towards antimony: bismuth is first positive towards copper, and afterwards negative. (Fechner.)

Platinum is very feebly positive towards gold in concentrated hydrochloric acid. (Walcker, Fechner.)

When copper or silver is fastened to anthracite by means of a wire under strong hydrochloric acid, dichloride of copper in tetrahedrons or chloride of silver in transparent octohedrons, is after a time deposited on the metal which remains positive—while carburetted [?] hydrogen gas is evolved at the surface of the anthracite. (Becquerel.)

Platinum is strongly positive towards peroxide of manganese, chlorine being evolved and chloride of manganese produced.

Electrical series of metals in hydrochloric acid, according to Faraday: Zinc, cadmium, tin, lead, iron, copper, bismuth, nickel, silver, antimony.

Experiments with Oil of Vitriol. In fuming sulphuric acid, zinc is first negative towards lead, then neutral, then positive.—Zinc is negative to tin and remains so on moderate dilution of the acid; whereas fresh zinc in the same mixture would be positive towards tin:—zinc or tin is positive towards iron;—bismuth positive towards zinc, lead, or antimony;—bismuth towards tin, first positive, then negative. (Fechner.)

A pair of zinc and copper in oil of vitriol produces a current which, together with the accompanying development of gas on the zinc, soon ceases. Breaking the circuit does not restore the current: agitation on the surface of the zinc restores it partially; but a drop of water on the

e [which dissolves the incrusting sulphate of zinc] immediately a current and an evolution of gas. (Rosenschöld.)

inc heated by itself in oil of vitriol to 240° dissolves quickly, with lution of hydrogen and sulphurous acid gas; brought into contact with latinum, it takes three times as long to dissolve,—and the gas, which is wholly evolved on the surface of the platinum, is nearly pure sulphurous acid. (Andrews.)

Lead in oil of vitriol remains positive towards platinum for eight days. (Pfaff.)

Silver in oil of vitriol is positive, gold negative towards platinum. (Walcker.)—Charcoal is negative towards platinum. (Walcker.)—Charcoal is very strongly positive towards platinum when the oil of vitriol is heated to between 100° or 150°, at which temperature the charcoal is powerfully attacked by the acid. (De la Rive.)

Experiments with Dilute Nitric Acid. Zinc is strongly positive towards cadmium.—Iron and nickel are permanently positive with copper, antimony, and bismuth. (Faraday.)—When zinc is connected with metallic lead in a mixture of one part nitric acid of 1·3 sp. gr. and 4 parts water, a portion of lead is dissolved as well as zinc; and, if the zinc be in the upper part of the liquid, a lead-tree is formed. (Runge.) [Were the metals in intimate contact?] Lead is positive towards iron and copper, and is very strongly acted upon when joined with them.—Gold and platinum when united give no current at first; but when they have been kept separate for some time in the acid and are then united, the gold becomes positive. (Becquerel.)

Platinum is positive towards peroxide of lead, the current continuing till all the peroxide of lead has disappeared. (Schönbein.)

Electrical series according to De la Rive: Zinc, tin, mercury, lead, iron, peroxide of iron, copper, silver.

According to Faraday (one measure of concentrated nitric acid with 7 of water): Zinc, cadmium, lead, tin, iron, nickel, bismuth, antimony, copper, silver.

Experiments with Concentrated Nitric Acid. Many metals when immersed in this acid undergo a change of state; they become more electro-negative, less oxidable, and lose, either wholly or for the most part, their tendency to decompose acids and metallic oxides; they pass from their ordinary *active* state into a *passive* state. This was first shown by Keir, with respect to iron immersed in solution of nitrate of silver or fuming nitric acid; and the subject was followed up by Herschel, Wetzlar, Faraday, Mousson, Andrews, and particularly by Schönbein. It is probable that some of the facts relating to this matter may not be of galvanic nature; but they are so closely connected with galvanism, that it would not be convenient to consider them apart from that subject.

Zinc cannot be rendered permanently passive. So long, however, as it is kept in contact with platinum in nitric acid of 1·5 sp. gr., it dissolves much more slowly than under ordinary circumstances. (Andrews.)—In strong nitric acid, it is powerfully negative towards cadmium. (Faraday.)

Tin in the shape of foil undergoes no change in nitric acid of 1·5 sp. gr., even when boiled for 10 minutes; whereas dilute nitric acid immediately converts it into the hydrated peroxide, the action being attended with violent heat and evolution of gas. When tinfoil is dipped into acid of 1·5 sp. gr., and then taken out, oxidation begins after a few seconds at a single point, and spreads rapidly over all the parts that have

been wetted. This oxidation is not brought about by the moisture of the air or by the oxygen contained in it: for it likewise takes place in air dried by chloride of calcium, or in hydrogen gas. Hence the strong acid does not oxidize tin when it covers that metal in large quantity, but readily when spread over it in a thin film. (Schönbein.) [But crumpled tinfoil wetted with a very small quantity of nitric acid likewise remains unattacked.]

In nitric acid of such a strength as not to attack iron, but to act rapidly upon tin, the latter remains almost passive—if, before immersion, it be connected, either immediately or by the galvanometer, with a previously immersed strip of platinum. Positive electricity then goes from platinum through the galvanometer to the tin, and small pieces of oxide separate from the latter. The tin thus treated remains passive even after being separated from the platinum; but if the slightest motion be given to it, or if the part of the metal which projects from the liquid be wetted with nitric acid, rapid oxidation soon begins. (Mousson.)

Nitric acid of 1·5 sp. gr. does not act upon tin, even when the metal is immersed in it for weeks; acid of 1·47 sp. gr. acts violently. But when acid of the last mentioned strength is contained in a platinum vessel, and a piece of tin is introduced into it in such a manner as to touch the platinum before immersion, the tin becomes passive and remains so after being separated from the platinum. (Andrews.)

Tin in contact with platinum in concentrated nitric acid gives merely a transient current when agitated. (Faraday.) By immersion in nitric acid in connection with platinum, tin is rendered negative towards all metals excepting platinum. (Buff.)

Lead is at first negative towards copper in concentrated nitric acid, afterwards positive. (Fechner.) Towards copper it is negative. (De la Rive.)

Bismuth immersed in nitric acid of 1·5 sp. gr., immediately becomes passive, so that a small piece of it does not dissolve completely for several weeks. In acid of 1·4 sp. gr. it dissolves rapidly with effervescence; but on touching it with platinum, this action ceases, and the metal acquires a peculiar lustre. If the platinum be then removed, the bismuth sometimes becomes active, sometimes passive. In the latter case, it first becomes covered with a dark film, which subsequently dissolves,—the metal once more acquiring a bright surface and dissolving very slowly. As often as this passive bismuth, while under the acid, is touched with platinum, and then separated, the black film again appears, but is succeeded immediately by the former lustre. Without the aid of platinum, also, a piece of bismuth (weighing ½ grain) will often, when immersed in nitric acid of 1·4 sp. gr., begin to dissolve with effervescence, and then suddenly become passive, especially when the liquid is agitated. If melted bismuth be poured into a glass tube and filed through (in the tube) after cooling, the filed surface will be passive from the beginning in acid of 1·4 sp. gr. Bismuth also becomes passive in acid of 1·4 sp. gr. when used as the positive pole of a battery of two pairs of plates. (Andrews.)

Bismuth becomes as completely passive when placed by itself in strong fuming nitric acid as in acid of 1·4 sp. gr., in contact with platinum. It then produces no evolution of gas in acid of 1·4 sp. gr., but dissolves gradually, and exhibits a positive reaction towards platinum, when connected with it through the medium of the galvanometer.—In acid of 1·5 sp. gr., bismuth does not dissolve in the slightest degree; nevertheless it does not become passive,—for, on being subsequently put

acid of 1·4 sp. gr. it dissolves as rapidly as under ordinary circumstances. —The black film and subsequent brightening of the surface of bismuth in acid of 1·4 sp. gr. are produced, not only when the metal is touched with platinum, but likewise when the acid or the bismuth is moved with a glass rod. As long as the black film remains, the solution of the bismuth goes on slowly; and as long as the bismuth remains in contact with the platinum, gas is evolved at the surface of the latter [Nitric oxide gas?] (Schönbein).

The rapid solution of bismuth in acid of 1·2 sp. gr. is immediately checked by contact with platinum; but the bismuth still continues to dissolve, though slowly and without effervescence; it becomes black, and is positive towards platinum. Even when separated from the platinum, it dissolves but slowly. (Noad.)

In fuming nitric acid, bismuth is first negative towards lead, then positive, then permanently negative. (Fechner.)

Iron may be rendered *passive* in the following ways:

P. 1. By heating it in the air till it becomes coated with black oxide. (Herschel, Schönbein.) When one end of the wire is heated till it oxidates, the other end, which does not appear to be altered, is also rendered passive. (Faraday.)

P. 2. By dipping it for a short time into fuming nitric acid (Keir), or nitric acid of 1·5 sp. gr., or into a mixture of nitric acid of 1·35 sp. gr. and oil of vitriol (Schönbein), in which liquids it produces no evolution of gas, even from the beginning.

P. 3. By immersion in nitric acid of sp. gr. 1·399, in which it at first becomes brown and evolves red vapours, but afterwards acquires a bright metallic lustre. Sometimes it acquires a brown surface when thus treated; but if withdrawn for a moment from the acid and allowed to fall in again suddenly, it becomes passive in half a second and acquires the metallic lustre. With a somewhat weaker acid, convulsive intermissions of effervescence and inaction succeed one another at intervals of half a second or less—the effervescence, and subsequently the tranquil state, progressing from one end of the wire to the other. (Herschel.)

P. 4. A wire is dipped into acid of 1·35, which acts violently on it, taken out after a second, then put in again, and so on. After from four to six immersions and extractions, it becomes more passive than P 5. (Schönbein, Buff.)—In acid of 1·3 sp. gr., iron may also be made passive by repeated immersion and extraction, and likewise by agitating the liquid for some time. (Mousson.)

P. 5. In a mixture of one part nitric acid of 1·399 sp. gr. and ½ part water, iron, which acts violently, is placed in contact with platinum: the action is immediately stopped (in weaker acid the iron does not lose its activity). *Herschel.*—Generally speaking, the acid acts in two ways, violently or slowly, according to its strength. The violent action which takes place in the weaker acid is not interrupted by platinum. (Buff.)—Or platinum is first immersed in acid of 1·35 sp. gr.—then, iron which has previously touched the platinum: no solution takes place. Likewise, when a small piece of gold-leaf is fastened to the end of the wire, or a trace of platinum precipitated upon it by momentary immersion in solution of chloride of platinum, the iron is rendered passive by subsequent immersion in acid of 1·35 sp. gr. But combination with platinum has no effect in acid of 1·35 sp. gr. heated to 75° [C.?], or in mixtures of one part acid of 1·35 sp. gr. and from 1 to 1000 parts of water. (Schönbein.) If the iron be connected with platinum through the galvanometer,—then,

on immersing the metal in the acid, positive electricity goes abundantly at first, and sparingly afterwards, from the platinum, through the galvanometer, to the iron. The iron does not become completely passive till the current has reached its minimum. If its connection with the platinum be interrupted before this takes place, the iron spontaneously loses its passive condition in the acid, and is not afterwards capable of making another piece of iron passive (according to P. 7.) *Buff.*—Iron is also rendered passive by platinum, gold, graphite, or charcoal, in acid of 1·3 sp. gr. Silver acts less powerfully.—A steel needle dissolves, when first introduced into acid of 1·3 sp. gr., but subsequently becomes passive, from the action of the graphite which separates from the steel. (Faraday.) In acid of 1·204 sp. gr. an iron wire is not protected by being bound round with platinum wire, but, on the contrary, dissolved more quickly than it would be if alone. But if the platinum wire be first immersed in the acid, and then the iron wire bound round with it, the iron becomes passive, and remains so even when the platinum is removed—but in so slight a degree, that it is not capable of imparting (as in P. 7.) the passive state to another iron wire, but on the contrary renders it active. (Noad.) —If the positive electricity of a voltaic pile be transmitted through an iron wire, and the negative electricity through a platinum wire, into solution of acetate of lead, the iron acquires a coating of peroxide of lead (which acts like platinum), and is thereby rendered very passive in nitric acid. (Schönbein.)

P. 6. The positive electricity of a voltaic pile is conducted into nitric acid of 1·35 sp. gr. through an iron wire, which is dipped in last, after all the other parts of the circuit have been put in connection,—the negative electricity being conducted by a platinum wire. If the iron is immersed before the platinum wire, it does not become passive, but continues to dissolve. (Schönbein.)

P. 7. By communication: One end of a wire being rendered passive (P. 1) by ignition, this end dipped first into acid of 1·35 sp. gr. and then the end which is yet active, the latter also becomes passive. Similarly, with two wires connected without the acid—the ignited wire being first immersed, then the active wire. If the two wires are connected through the medium of the galvanometer, positive electricity goes for a short time from P. 1, through the galvanometer, to the active wire (Schönbein).—P. 5 is likewise sufficiently passive to impart the passive state to active iron (Faraday); so likewise is P. 4 (Buff):—If the end of the iron wire covered with peroxide of lead (*vid.* P. 5) be immersed in acid of 1·3 sp. gr., and then the active end, the latter will become passive; so likewise will another iron wire connected with it. (Schönbein.)

If the ignited end of the wire be dipped into the cup *a* (*App.* 2), the unignited end into the cup *b*,—*a* and *b* being filled with nitric acid of sp. gr. 1·3, and connected with a short wick of asbestus saturated with the same liquid,—the unignited end will remain active, on account of the dilution of the liquid. Similarly, when a platinum wire is substituted for the asbestus *h*; but if the connection *h* consists of copper or brass, or if only the immersed end of *g* consists of copper or brass, and the immersed end *l* of platinum or gold,—or if *h* consists of an iron wire—the end which dips into *b* having been ignited,—then, on first immersing the metallic arc *g i*, afterwards the ignited end *o*, and lastly, the unignited end *o p* of the iron wire,—the end *p* becomes passive.—If the ignited and unignited ends of the iron wire *o p* be first immersed in the cups *a b*,—then the *ignited end i* of an iron wire made to dip into *b*, and lastly the unignited

ito *a*, this end will become passive. If the wire *g h i* be active at ends, and it be dipped, after the immersion of the wire *o p*, first the end *i* in *b*, then with *g* in *a*,—*i* will immediately become pas- *e*, the end *g* remaining active. In this manner, several wires may be mersed one after the other, and made passive at the immersed end *b*. ut if the end of the iron wire *o p*, which dips into *a*, has been rendered assive, not by ignition, but by the action of nitric acid (P. 2 or P. 5),— hen, on connecting the cups *a b* in the manner above described, by means of an active iron wire, all four ends become active. (Schönbein.)

Iron rendered passive by nitric acid exhibits a brighter lustre than before. (Schönbein.) P. 1 conducts a feeble thermo-electric current perfectly well; iron made passive by nitric acid conducts it less readily; but the current of a galvanic circuit is conducted by the latter perfectly well. (Faraday.) [The scale oxide of iron, with which P. 1 is encrusted, is a very good conductor; specular iron, which probably envelopes iron made passive by nitric acid, does not conduct so well (p. 310).]—Noad concludes from his own experiments that iron made passive by nitric acid cannot be regarded as a conductor, even for the galvanic current.

P. 3 is no longer attacked by nitric acid of 1·399 sp. gr., not even after being washed with water and ammonia, or exposed to the air, or gently touched, either in or out of the acid, with glass, gold or platinum; but brisk rubbing renders it active, and effervescence ensues, continuing till the iron has resumed its passive state. It likewise becomes active by being touched under the acid with zinc, antimony, bismuth, lead, or copper, the effervescence spreading out from the point of contact over the whole of the immersed part.—If the middle of the wire, P. 3, be covered with wax, both ends dipped into the same acid, and one touched with copper, both become active; but if the end not touched by the copper projects above the acid, the end in contact with the copper alone becomes active. (Herschel.)

P. 3 withstands the action of nitric acid tolerably dilute; also that of acid of 1·399 sp. gr. pretty strongly heated, but not that of boiling acid; whereas P. 1 is not soluble even in boiling acid. (Herschel.)

Iron wire made passive by ignition is rendered active again by rubbing. (Faraday.)

Iron made passive by fuming nitric acid remains so, even when exposed to the air for several hours or even days. (Schönbein.)

Iron rendered passive by nitric acid loses its passive condition completely when all the acid is washed off. (Buff.)

Passive iron is attacked by chlorine gas, bromine vapour, and hydrochloric acid, and regains its active condition. (Schönbein.)

Iron made passive in nitric acid regains its activity when it is taken out of the acid, and the adhering acid removed by evaporation. The wire, while still wet, remains passive in contact with glass, wood, paper, platinum,—but becomes active by contact with oxidable metals: these produce at the point of contact a dark stain of oxide, which diffuses itself over the whole wire. (Mousson.)

P. 1 is passive towards nitric acid of 1·35 sp. gr. even when heated; but if subsequently heated in hydrogen gas, it recovers its activity. Iron wire plunged in a state of ignition into nitric acid of 1·5 sp. gr., gives up no iron to it, even after 5 minutes' boiling. Iron does not dissolve in acid of 1·5 sp. gr. even at a boiling heat [?].—P. 2 does not dissolve in acid of 1·35 sp. gr. even boiling [?].—If P. 2 be washed with water, it is attacked with violence by acid of 1·35 sp. gr.—Passive iron does not

dissolve in ordinary nitric acid, even when kept in it for years, unless the temperature be near the boiling point. In dilute sulphuric acid—on the contrary—*e. g.*, 1 part acid of 1·35 to 10 parts water—all passive iron becomes active and dissolves;—in the case of P. 1, the crust of insoluble oxide peels off at the same time. But when made to form the positive pole of the voltaic pile, it remains passive in the most dilute nitric acid, and in other oxygen acids (*vid. Decompositions by the electric current*). P. 2 is passive in a mixture of 1 part of hyponitric acid with 10 parts of water, but may be rendered active by slight agitation. (Schönbein.) P. 5 heated in contact with platinum in acid of 1·3 sp. gr. dissolves rapidly, but not till the temperature is raised nearly to the boiling-point. (Faraday.)

P. 1, 2, 5, or 6 retains its passivity better than P. 7, which may be made active, not only in heated or dilute acids, but likewise in the following ways: *a*. When the part which has been in the acid is taken out and strongly agitated (agitation in the acid has no effect).—*b*. When two such wires are rubbed together at the part in which they touch the surface of the acid.—*c*. When the end which has been taken out of the acid is touched by a metal which decomposes the acid, such as tin, zinc, iron, copper.—*d*. When P. 7 is touched by such a metal within the acid, or two ends of P. 7 connected outside the acid with the other metal, whilst the two other ends are immersed. (Touching P. 7 with phosphorus oxidizing in the acid does not destroy the passive state.) (Schönbein.)

On dipping first the unignited and then the ignited end of a wire into acid of 1·35 sp. gr., the latter becomes active. If active and passive iron P. 1—7 be dipped separately from each other into nitric acid of 1·35 sp. gr., and then connected, the passive iron becomes active. (Schönbein.)

Passive iron becomes active when touched, under nitric acid of 1·35, with an oxidable metal, such as zinc, tin, lead, active iron, copper, brass, and even with passive bismuth; but if it be at the same time in contact with platinum, it is not rendered active by passive bismuth. (Schönbein.)—When passive iron is connected with an oxidable metal through the medium of the galvanometer, instead of in the acid, positive electricity goes from the iron through the galvanometer to the latter. (Mousson.)

If an active iron wire in the form of a fork *a b* (*App.* 17) be connected at *c* with a straight wire *c d*, whose other end, *d*, has been ignited, and this end be first dipped into acid of 1·35 sp. gr., then the ends *a b*, the latter will also become passive. But if the end *b* be connected with an active wire *e b*, the effervescence will progress from this end to the end *b*, but not to the end *a*; except when the connection between *a b* and *c d* is broken. (Schönbein.)

When iron wire made passive by nitric acid is connected by means of the galvanometer with an active wire of iron or steel, and dipped into acid of 1·3 sp. gr., it sends positive electricity through the galvanometer to the active wire, a short time after immersion; upon this, the passive wire is dissolved and the current ceases. If one wire be touched in the acid with gold, platinum, or charcoal, both wires become passive. (Faraday.)

On connecting an active and a passive wire with the galvanometer, and immersing, first the passive, then the active wire in acid of 1·374 sp. gr., a large quantity of positive electricity passes, at first, from the passive wire through the galvanometer to the active wire: the passive wire then also begins to dissolve; finally, both wires become passive and the current

ceases. But as soon as one of the wires is touched with copper or active iron, it becomes itself active, and generates a new current. (Noad.)

Pulsating action. A wire, P. 4, immersed in acid of 1·35 sp. gr. at a temperature between 12° and 15°, and placed in contact for a short time with a copper or brass wire, acquires a slow and intermitting activity. Similarly, the two ends of a fork-shaped wire, P. 4,—one end being in contact with copper or brass—become intermittingly active (*i. e.* liberate gas) at intervals of a second, then again passive, and so on for several alternations,—after which they generally become permanently active, the activity extending itself from the surface of the acid to the lower part of the wire. In other cases, these intermissions are succeeded by a permanently passive state, which is again interrupted by contact with copper, and invariably passes into the permanently active state by continued contact with copper.—If several wires are brought into the pulsatory condition in the same liquid, their pulsations do not coincide, unless they touch one another.

The higher the temperature of the acid, the greater is the difficulty of inducing the pulsation: above a certain degree of heat, copper immediately induces the permanently active state. Water added to the acid during the pulsation always increases its rapidity, and still further dilution renders the activity permanent. (Schönbein.)

When the pulsating condition is produced in acid of 1·3 sp. gr. by contact with a very fine copper wire, a dark film of oxide is observed to commence at the point of contact, and extend itself in all directions over the wire; gas is evolved on the part of the wire thus covered, and the wire behind it recovers its metallic lustre:—then a second dark film is produced, attended with evolution of gas—and then the bright state reappears without evolution of gas,—and so on. (Mousson.)

To the experiments here enumerated, I shall further add some of my own:

Experiments with Iron Wire and Acid of 1·5 *sp. gr.* Wire which is passive in the cold, begins to evolve gas somewhat under 80°; at 100°, the evolution of gas goes on quietly and uniformly, and the acid becomes so strongly charged with oxide of iron, that it becomes syrupy, and, on cooling, solidifies into a yellowish brown fibrous mass (which, when dissolved in water, deposits brown flakes on boiling).—If the acid be heated to violent ebullition in contact with the wire, it assumes the pulsating state, sometimes immediately, sometimes after long boiling. A bundle of wires may also be brought into this state by heating the acid even in the water-bath, because the solution of the large quantity of iron furnished by the wires raises the temperature. Pulsating wire produces, at 100°, a stronger evolution of gas than wire not in that condition; the evolution of gas gradually increases from above downwards (sometimes the reverse), and after a time experiences a sudden augmentation, attended with the formation of large bubbles,—sometimes causing the acid to be thrown out of the vessel: it then diminishes, and, after a corresponding interval, again rises almost to explosion, and so on. The intervals are shorter in proportion as the acid is less charged with iron; with acid very much saturated, the pulsation is less evident.—When the pulsating and the active end of an iron wire are immersed in acid at 100°, the former often pulsates for a time by itself, then the other end also, and both in equal times.—If the wire be taken out before the pulsation begins, the pulsating end immediately becomes covered with a brown film, whilst the other end remains bright; but after pulsation, both ends become brown

on exposure to the air. When a pulsating and a non-pulsating wire are connected with the galvanometer, the former is found to be positive, at 100°, towards the latter. The deflection increases till pulsation begins, upon which the needle suddenly retrogrades. (Gm.)

Experiments with Iron reduced from the state of Peroxide by Hydrogen gas. A large quantity of finely divided iron introduced into a small quantity of nitric acid of 1·5 sp. gr. produces a violent effervescence. This effect is kept up for some time, in consequence of the rise of temperature which ensues, but gradually diminishes as the liquid cools; so that a large quantity of iron remains undissolved: this, however, disappears completely on heating the acid in the water-bath. Finely divided iron, sifted by small quantities at a time into acid cooled by snow, produces effervescence on each addition; this, however, soon ceases,—so that a large quantity of iron may, by little and little, be introduced into the acid without causing any considerable action. If the acid be now poured off, and water poured upon the powder, violent effervescence ensues. But if the powder be freed from adhering acid, by transferring it to a plate of gypsum, and, when nearly dry, introduced by small portions at a time into water which has been boiled and cooled, it will, when thus washed, communicate a deep red colour to a mixture of hydrochloric acid and sulphocyanide of potassium (which colour gradually disappears as the metallic iron dissolves),—whereas, reduced iron not treated with nitric acid scarcely reddens the same mixture. If the powder, freed by gypsum and water from adhering acid, be dried in a glass tube by a current of dry hydrogen gas, continued for several days, first at the ordinary temperature, then at gentle heat, and finally heated to redness in the stream of gas,—a considerable quantity of water is immediately deposited. [The hissing noise caused by the powder even in concentrated nitric acid, the experiment with sulphocyanide of potassium, and that with hydrogen gas, are in favour of the supposition that a film of peroxide of iron is formed.] (Gm.)

[The passive condition of iron treated with nitric acid, nitrate of silver, &c. probably arises,—according to Faraday's earlier view (which, however, he has subsequently modified, *Phil. Mag. J.* 10, 75),—from the formation of a thin film of anhydrous oxide of iron, analogous to specular iron. This view is supported by the fact that iron which has been ignited, and is therefore completely covered with black oxide ($Fe^3 O^4$), exhibits precisely the same characters,—excepting that, from the greater thickness of the coating, its passive condition is more complete,—and that iron becomes passive only in liquids which readily give up oxygen. So thin a film of specular iron cannot destroy, but merely modify, the lustre of the metal. Now this coating almost wholly resists the solvent action of cold strong nitric acid; hence it prevents the acid from coming in contact with the rest of the iron, and consequently its further action. When the acid is heated, and partly dissolves off the coating, a new one is immediately formed by its action on the exposed iron. In acid of 1·5 sp. gr. the formation of this coating takes place immediately; in acid of 1·35, contact with platinum, &c. is necessary, the second metal serving to convey the negative electricity set free in the iron to the nitric oxide, and thereby facilitating the combination of the iron with the oxygen of the acid (p. 341, *k*). A similar effect is produced by the electric current of a voltaic battery, if the iron conveys positive electricity into the nitric acid. Oxidable metals, on the contrary, such as copper, destroy the *passive state of iron*: for while they take up the oxygen of the nitric acid,

they conduct negative electricity to the iron, towards which, therefore, the nitric oxide is transferred; and thus coming in contact with the film of oxide, decomposes it by abstracting its oxygen. Iron which is highly passive—especially that which has been ignited, and is therefore covered with a thick film of oxide—is capable of inducing the passive state in iron which is connected with it,—acting in fact like platinum; it is true that it hereby loses a portion of its covering of oxide, just as it does when in contact with copper; but since this coating is of considerable thickness, the other iron becomes passive, sooner than that which is already passive can be rendered active. On the other hand, iron less completely passive becomes active by connection with iron already in a state of activity,—inasmuch as it loses its passive character before the active iron has acquired a coating of oxide sufficient to render it passive. Dilute nitric acid, hydrochloric acid, all acids, in short, by which oxide of iron is easily dissolved, destroy the passive state by removing the oxide. The remarkable phenomena of pulsation must, on this hypothesis, be attributed to the rapid formation and subsequent solution of the film of oxide. Even if complete explanation be unattainable at present, it may yet be hoped that this mode of explanation—which is likewise applicable to the other passive metals—will, on more exact investigation, be found to embrace the whole of the facts relating to the passive condition of iron.—Mousson attributes the passive state of iron to a covering of nitrous acid; Wetzlar and Schönbein to a peculiar electro-dynamic condition into which they suppose the iron to be brought.]

In concentrated nitric acid, iron is negative towards antimony, bismuth, copper, and silver,—positive towards gold and platinum. (Fechner.) —In nitric acid of 1·5 sp. gr. positive electricity passes at the first moment from the platinum through the galvanometer to the iron; but the current soon ceases. (Mousson.)—In concentrated nitric acid [possibly not the strongest], iron is positive towards lead, and is violently attacked. Towards copper it is often negative at first; but, with the suddenly commencing rapid solution of the iron, the current is reversed. (De la Rive.)—Passive iron is negative towards active iron, copper, and silver. (Buff.)

Active iron in concentrated nitric acid is positive for the first instant towards copper and silver, but soon becomes negative, and remains so. In acid of 1·3 sp. gr., active iron is at first positive towards silver, becomes negative for a few seconds, then again positive, and so on alternately eight or nine times, till at length it becomes permanently positive. Passive iron is negative towards silver in acid of 1·3 sp. gr.; but the action continually diminishes in energy, and finally ceases when the surface of the silver becomes tarnished. (Faraday.)

Passive iron is feebly positive towards platinum in concentrated nitric acid. (Schönbein.) Active iron is at first strongly positive towards platinum in acid of 1·3 sp. gr.; but the current soon ceases, as the iron passes into the passive state. Passive iron, therefore, gives no current with platinum, even when first immersed in the acid; but whenever the iron is moved, a momentary current is excited. Steel in concentrated nitric acid remains strongly and permanently positive towards platinum for fourteen days, but is not attacked by the acid. (Pfaff.)

If an iron wire coated with peroxide of lead (by precipitation from solution of acetate of lead in the voltaic circuit) be connected, through the medium of the galvanometer, with an active iron wire, and both wires immersed in nitric acid of 1·3 sp. gr., positive electricity will pass

—though for a short time only—from the coated wire, through the galvanometer, to the other wire, which becomes passive. A feeble current probably continues in the same direction; the peroxide gradually dissolves; and as soon as the last trace of it disappears, the iron begins to dissolve also. (Schönbein.)

Nickel is negative with copper, bismuth, and antimony in strong nitric acid; with silver it is at first positive; then, as it becomes coated, negative. (Faraday.)

Copper may be rendered passive in the same manner as bismuth, so that it will dissolve but slowly in acid. It immediately becomes passive in acid of 1·5 sp. gr.; in acid of 1·47 sp. gr. it is at first violently acted upon, and then becomes passive. If previously connected with platinum, it assumes the passive condition immediately, and retains its lustre as long as the contact lasts. On the removal of the platinum, the copper becomes covered with a black film, which is not completely removed either by the action of the acid, or by renewed contact with platinum.—In acid of 1·4 sp. gr. contact with platinum restrains the rapid solution of the copper, and imparts a shining surface to it. When the platinum is removed, the copper becomes covered with black oxide, which dissolves slowly; and passive copper, possessing a bright metallic lustre, remains. If the copper be taken out of the acid while yet covered with oxide, the acid still adhering to it rapidly dissolves the oxide, leaving the copper in the active state. (Andrews.)

A thin copper wire surrounded with platinum wire remains bright in strong nitric acid, but dissolves on the removal of the platinum. If both the copper and platinum wires are connected with the galvanometer, and dipped into the acid, a few bubbles of gas make their appearance—at the beginning only—on the surface of the copper, and a stronger current is excited; but the rapid solution immediately ceases, and only a feeble, though constant, current remains. (Mousson.)

Copper is positive towards bismuth and antimony in strong nitric acid. (Fechner.)—It is positive towards lead, and is at first violently attacked, exhibiting, therefore, the reverse of its action in dilute acid. (De la Rive.)—Towards platinum it is highly positive (the deviation amounts to 90° in nitric acid, and to 40° in oil of vitriol). (De la Rive.)

Gold gives no current with platinum in pure nitric acid. But if the gold contains copper, or if a drop of hydrochloric acid or solution of common salt is added to the nitric acid, chemical action takes place upon the gold, and that metal becomes positive. (Becquerel, De la Rive.) Gold is likewise positive towards platinum in chlorine water. (Ritchie, *N. Ed. J. of Sc.* 2, 150.)—In pure nitric acid, also, gold is feebly positive towards platinum. (Fechner, Marianini.) (As Marianini's experiment was made at Venice, the sea air may have introduced a trace of alkaline chloride into the acid. *De la Rive.*)—Platinum gives a current with rhodium in nitric acid, only on the addition of hydrochloric acid,—the platinum is then positive. (De la Rive.)

Platinum is negative towards anthracite in nitric acid. (Becquerel.)

Platinum is highly positive with peroxide of manganese in strong nitric acid, oxygen gas being evolved. (De la Rive.) It is still more highly positive in nitric acid mixed with alcohol, or in a mixture of hyponitric acid with an equal quantity of water; in the last case, the peroxide of manganese gives up oxygen to the hyponitric acid. (Faraday.)

Platinum is positive in nitric acid towards peroxide of lead, which at *the same time* gradually disappears (it is likewise slowly soluble in nitric

acid when alone); also with red lead. (De la Rive, Faraday, Schönbein.) Yellow oxide of lead and white lead, on the contrary, are positive towards platinum, because they do not give up any oxygen. (Faraday.)—Passive iron also is strongly positive towards peroxide of lead in concentrated nitric acid. With peroxide of silver in concentrated nitric acid, platinum is somewhat more positive than with peroxide of lead; and the latter is positive towards peroxide of silver, because the last-mentioned oxide gives up its oxygen more readily. (Schönbein.)

Electrical series in nitric acid of 1·48 sp. gr.: Cadmium, zinc, lead, tin, iron, bismuth, copper, antimony, silver, nickel. (Faraday.)—In nitric acid of 1·5 sp. gr.: Passive iron, platinum, peroxide of lead, peroxide of silver. (Schönbein.)—In concentrated acid: Tin, zinc, iron, copper, lead, mercury, silver, peroxide of iron. (De la Rive.)

Experiments with Aqueous Solution of Potash or Soda. Potassium or sodium is positive towards zinc in concentrated solution of potash. (H. Davy.)

Amalgamated zinc neither dissolves nor causes any evolution of gas in solution of potash: as soon as it is connected with platinum, hydrogen gas is evolved at the surface of that metal, but more slowly than in dilute sulphuric acid, the quantity of gas being in stoichiometrical proportion to that of the zinc dissolved (32·5 parts of zinc to 1 part of hydrogen). (Faraday.)—When zinc is left for 20 hours in a solution of one part of hydrate of potash in 4 parts of water, the weights which it loses when alone, when connected with platinum, and when connected with iron, are as 1 : 11 : 148. Hence, iron exerts the strongest action; and the quantity of hydrogen gas evolved at its surface is abundant in proportion. (Runge, *Pogg.* 16, 129.)—Zinc gives in solution of potash a more powerful current with iron, than with copper, silver, or platinum. (Poggendorff.)

Bismuth and antimony in caustic potash are positive towards nickel. (Faraday.)—Tin is positive towards iron in caustic potash or lime-water. (J. Davy.)—Polished lead is positive towards iron in caustic potash or lime-water; tarnished lead negative. (Yorke.)—Tin and iron are positive towards copper in solution of potash. Iron joined with platinum in solution of potash produces no current, and remains as bright as if it were placed alone in the liquid; it merely becomes oxidated at the end which projects out of the liquid. (De la Rive.)—Iron in caustic potash is first positive towards copper, afterwards negative; with platinum it is positive,—more strongly, in proportion as the platinum is immersed for a longer time before the iron,—less strongly, in proportion as the iron is immersed alone for a longer time. (Fechner.)—Iron or nickel gives with platinum, in concentrated solution of potash, a very feeble current, which soon diminishes, the platinum being the negative metal. In a dilute solution, the current is likewise very feeble, but continues for a longer time. (Faraday.)

With silver and platinum the current is scarcely perceptible in a concentrated solution, and absolutely nothing in a dilute solution. (Faraday.) —Silver gives no current with platinum in alkaline liquids. (De la Rive.) —When copper is connected with silver or platinum in strong solution of soda—the latter being immersed first—the copper is strongly negative at the beginning of the action, but soon becomes positive. Silver exhibits a similar action with platinum—whereas, in a dilute solution of soda, it is positive from the beginning. (Walcker.)—Gold with platinum in solution of potash continues positive for several days. (Pfaff.)

Platinum is positive with peroxide of manganese in solution of potash

(De la Rive, Faraday); more strongly on the addition of alcohol (which exerts a deoxidizing action on the peroxide of manganese). *Faraday.*

Arsenic is strongly positive towards iron in fused hydrate of potash (the contrary in acids). *De la Rive.*

Electrical series in aqueous solution of potash or soda: The alkali-metals and their amalgams, zinc, tin, lead, copper, iron, silver, palladium, gold, platinum. (H. Davy.)—In solution of potash, either strong or weak: Zinc, tin, cadmium, antimony, lead, bismuth, iron, copper, nickel, silver. (Faraday.)—In solution of potash or soda of sp. gr. 1·33: Tin, zinc, antimony, lead, copper, gold, platinum, bismuth, steel, silver. (Pfaff.)

Experiments with Ammonia. Steel becomes passive in a somewhat dilute solution of ammonia, but not for so long a time as in nitrate of silver. (Wetzlar.) [The existence of this passive condition is inferred by Wetzlar from his having observed that the bar of iron when taken out of the ammonia and dipped into a solution of sulphate of copper, does not begin to precipitate the copper till it has been immersed for about a minute. But the ammonia still adhering to the iron causes it to be surrounded with precipitated oxide of copper, and this prevents the action for a time.]

Zinc is positive towards tin and copper; tin and iron negative to copper. (De la Rive.)

Tin is positive towards copper at the first moment, but gradually becomes negative. (Fechner asserts the contrary.) The same relation is exhibited by iron towards copper,—excepting that in this case the reversal of the current takes place in a few seconds. (Marianini.) This change of direction is attributed by Marianini to the different degrees of alteration which ammonia produces in the surfaces of different metals: it makes tin more strongly negative than copper;—for, when two plates of tin are successively immersed in it, the one which is first immersed exhibits towards the other a stronger negative reaction than a copper plate, under similar circumstances, would exhibit towards another copper plate. Moreover, if the copper plate is immersed five minutes after the tin plate, the tin still appears positive at the beginning, but less strongly than when both metals are immersed at the same time. Lastly, if the two metals are separately immersed in ammonia for ten minutes, and then dipped into dilute acid or a solution of salt, the copper still remains constantly positive towards the tin.

Platinum in ammonia is strongly negative towards peroxide of manganese,—a yellow substance, probably the hydrate of a lower oxide, being formed at the same time. (De la Rive.)

Electrical series in aqueous ammonia of sp. gr. 0·95: Zinc, tin, lead, silver, copper. (Pfaff.)

Experiments with Aqueous Solutions of Alkaline Salts. In a solution of common salt, zinc gives a stronger current with iron, than with copper, silver, or platinum. (Poggendorff.)—Zinc, tin, and iron protect copper in sea-water perfectly. (Van Beek.)

Iron placed by itself in sea-water is strongly attacked; the greater the depth, however, the less is the corrosion, because the oxygen of the air has less access. If pieces of zinc are attached to the iron here and there, the iron is completely protected, and the zinc is not nearly so much corroded as the iron was before. Zinc likewise protects the iron as well as the tin of tin-plate, in sea-water. (E. Davy.)—Copper, on the contrary, is not completely protected by zinc in sea-water contai[illegible] (J. Davy.)

—Zinc completely protects iron in sea-water, the iron becoming covered with marine plants; but the zinc is quickly corroded. (Grant, *J. pr. Chem.* 7, 290.)—[Protection of cast-iron in sea-water by means of a coating of pulverized zinc. (Mallet, *J. pr. Chem.* 22, 352.)]

If the U-tube (*App.* 4) contains a solution of common salt, nitre, Glauber's salt, or sulphate of magnesia,—zinc, tin, or lead being immersed in one arm, and copper or platinum in the other, and the two metals being connected by the galvanometer,—the current diminishes after some time, but may be renewed by introducing a little acid into the vessel containing the copper or platinum; whereas the acid, if put into the arm containing the zinc, produces no current, although it causes a brisk disengagement of gas from the zinc. (Rosenschöld.) [The oxygen of the water and the acid of the salt are transferred to the zinc, the hydrogen of the water and the base of the salt to the copper. The layer of the base thus accumulating on the copper prevents the portions of base afterwards separated from coming in contact with the copper, and thereby receiving negative electricity from it. An acid added to the liquid saturates the separated base, and facilitates the access of the portions afterwards separated.]

If water containing carbonate of lime, held in solution by excess of carbonic acid, be placed in contact with zinc and copper, the whole of the carbonate of lime is deposited on the copper. When water of this nature flows through leaden pipes, the carbonate of lime is deposited at the joints (which are soldered with an alloy of tin and lead), on the brass cocks, and on any piece of iron or silver that may have been introduced, thereby producing stoppage. To prevent this accident, lateral tubes are adapted to the main pipe at intervals varying from twenty to thirty feet, and furnished with plugs of copper or tin, or still better of cast-iron, —and by means of these, the calcareous deposit is from time to time removed. (Dumas, *Ann. Chim. Phys.* 33, 266.)

A long copper wire is completely protected from the action of sea-water by a short zinc wire, the latter being quickly corroded.—If the copper and zinc are not in immediate contact, but separated outside the water by an extremely thin film of mica, or a sheet of common dry paper, the copper is not protected; but if they are kept apart by a sheet of thin silver paper, the protecting action is exerted.

When the bends of a long copper wire are immersed in eight vessels filled with sea-water, and connected by ropes saturated with the same water—the copper in the first vessel being placed in contact with zinc,—the copper in all the vessels is protected, if the ropes are 0·5 inch thick; but if their thickness is only 0·1 inch, the protection extends only to the third vessel. After some time, the copper in the first vessel becomes covered, partly with metallic zinc, partly, on the lower surface, with crystallized carbonate of soda and carbonate of lime,—that in the second vessel with fine crystals of carbonate of lime and a small quantity of carbonate of soda,—that in the third remains clean,—that in the fourth is somewhat attacked, but remains bright,—and the portions in the remaining vessels appear more and more corroded and covered with verdigris. (H. Davy.)

When a plate of tinned iron is immersed in sea-water, the iron oxidizes while the tin remains intact. (E. Davy.)—Steel and tin undergo no alteration in boiling sea-water; but in cold sea-water containing air steel becomes rusty (though not more so than under ordinary circumstances), while tin connected with it remains unaltered. In sea-water which has been well boiled, and then cooled, steel does not rust if access of air be prevented. Hence the rusting is due to the oxygen of the air. (J. Davy.)

—Iron in contact with tin in sea-water is negative at first, but becomes positive after a few minutes. It oxidates more quickly in sea-water when in contact with tin than when alone, and the tin remains bright,—whereas, when placed alone in sea-water its surface becomes tarnished. (Van Beek.)—A plate of iron, which, when immersed alone in sea-water, loses 181 grains, loses exactly 333 grains when placed in contact with tin under the same circumstances, while the tin loses only 5 grains. (Mulder.) —Cast-iron suffers greater loss in sea-water when connected with tin than when in contact with copper. (Mallet.)

Polished lead is positive towards iron and copper in a solution of nitre, but lead superficially oxidated is negative. (Yorke.)—Lead in solution of sal-ammoniac is at first positive towards iron, but the current is soon reversed. (Wetzlar.)—In solution of sal-ammoniac, iron is positive towards tin, and copper towards bismuth. Lead with iron is first positive, then negative.—In solution of common salt, bismuth is first positive towards copper, afterwards negative. (Fechner.)

The corrosion of the copper sheathing of ships may be diminished by fastening to it at several points pieces of cast or wrought-iron, called *Protectors*. A plate of copper on a sailing-ship—which, when unprotected, loses 6·55 grains in twelve hours—loses 5·5 grains when furnished with cast-iron protectors, whose surface is equal to $\frac{1}{300}$ of that of the copper, and 2 grains when the surface of the protectors amounts to $\frac{1}{100}$ of its own. Part of this loss arises from mechanical attrition. Ships furnished with protectors of cast-iron, whose surface was from $\frac{1}{100}$ to $\frac{1}{70}$ of that of the copper, returned from their voyage with much less loss of copper than when unprotected. The sheathing was sometimes quite clean, sometimes covered with carbonate of lime, marine plants, shells, &c.—especially in the neighbourhood of the protectors, where a large quantity of oxide of iron was deposited, and on the nails, which consisted of an alloy of copper and tin—this alloy being much more highly electro-negative than copper. This deposition on the copper sheathing is principally formed while the ships are in harbour. The surface of the protectors must, therefore, be of such extent as not completely to protect the copper. (H. Davy.)—In sea-water containing sulphuretted hydrogen, protectors of zinc may be used. (Daniell, *Ann. Chim. Phys.* 78, 339.)

If cast iron loses 1 part of its weight when immersed alone in sea-water, its loss when in contact with copper will amount in the same time to 1·4, and with an alloy of 1 At. zinc and 7 At. copper, to 1·5 of its weight. (Mallet.)

Copper dissolves in aqueous solution of bicarbonate of soda; iron united with it remains bright. (Wetzlar).

If silver be immersed in one arm of a U-tube (*App.* 4) containing solution of common salt, and platinum in the other, rhombohedral crystals make their appearance in a few months, being white at first, then violet, and afterwards blue; they do not change in water. (Becquerel.)

Platinum gives no current with tellurium, palladium, or rhodium in a solution of common salt, because no chemical action takes place. (H. Davy.)

Platinum is positive towards anthracite in solutions of sulphates or chlorides. (Becquerel.)

Electrical series in solution of common salt: Zinc, lead, tin, iron, antimony, bismuth, copper, silver, gold, platinum. (Fechner.)

Experiments with Aqueous Solutions of the Heavy Metallic Salts.—It

ften happens that one metal precipitates another from its solution in acid r alkali, the former taking oxygen from the latter, and dissolving in the tate of oxide in the acid or alkali. (*Sch.* 18.) The action is at first purely hemical; but as soon as a small quantity of the second metal has been recipitated on the first, electro-chemical action sets in. The precipitating netal—which of course possesses the greater affinity for oxygen—is the positive, and the precipitated metal the negative element of the circuit. n consequence of this action, the further deposition of the second metal akes place on the already precipitated portion of that metal; and thus rystalline vegetation or *Metallic Trees* (p. 136) are produced, the egative metal being ultimately deposited at a considerable distance from he positive one.

If a piece of iron wrapped up in bladder, silk, or paper, be immersed n a solution of blue vitriol, only a small quantity of copper will be leposited inside the envelope, the greater part—possessing the metallic ustre—collecting on the outside. (Mulder, *Br. Archiv.* 22, 291; *comp.* Bischof, *Schw.* 36, 119.)—When a solution of acetate of lead is decomposed by suspending a bar of zinc within it, the liquid in the neighbourhood of the zinc soon becomes free from lead—whilst that at the lower end of the growing lead-tree still contains lead in solution. (Rose, Pfaff.)—A piece of the lead-tree which may chance to fall off, gradually dissolves and is again precipitated on the zinc. Direct experiments show that lead (when access of air is allowed) dissolves in a saturated solution of chloride, nitrate, or acetate of zinc, a basic salt being probably formed at the same time. (Fischer, *Pogg.* 4, 291.)

Zinc and Tin Salts.—Zinc produces a strong current with copper in solution of sulphate of zinc, although the sulphuric acid may be already saturated with zinc—and therefore no chemical action can take place. (Pfaff.)—Zinc however causes an evolution of hydrogen gas when placed by itself in solution of sulphate of zinc [because a basic salt is produced]. (J. Davy.)—Zinc is deposited on copper placed in contact with zinc in solution of sulphate of zinc. (Grotthuss.)—Zinc, in the solution of its sulphate, produces a much feebler current with iron than with copper or platinum. (Poggendorff.)—In a saturated solution of sulphate of zinc or protochloride of tin, steel wire produces a feeble current with silver, the steel being positive;—no current with platinum. (J. Davy.) Since steel gives no current with platinum, J. Davy concludes that the electric current is not produced by chemical action. [I have found that steel wire produces with platinum about the same deflection as with silver, both in perfectly neutral sulphate of zinc and perfectly neutral protochloride of tin.]

Lead Salts. Active iron does not precipitate nitrate of lead, but becomes passive in it. (Keir.)—From a solution of acetate of lead, the lead is deposited on lead, silver, or gold, when these metals are placed in contact with zinc, tin, or iron.

Copper Salts. Copper is deposited from a solution of its sulphate, on silver, gold, or platinum placed in contact with zinc, tin, lead, iron, or—according to Grotthuss—even with copper.

If an amalgamated copper wire be made to dip into mercury, the surface of which is covered with solution of sulphate of copper, and a piece of amalgamated zinc made to dip into the copper solution, then—on connecting the two metals with the galvanometer—the zinc is found to be strongly and permanently positive, and the mercury becomes saturated with copper. (Grove.) [Oxygen from the oxide of copper is transferred with the acid to the zinc, and copper to the mercury.]

In a concentrated solution of sulphate of copper, tin and iron are positive towards lead; bismuth and copper nearly neutralize one another. (Fechner.)

Sulphate of copper and potash is not reduced by iron, except when the iron is connected with silver. Dilute solution of nitrate of copper scattered in single drops upon a clean rod of iron produces a deposit of copper at every point of contact; but if the solution is concentrated, only a few of the drops produce an immediate deposition, others in a few minutes, others again not for some hours, and others not at all. The precipitation may however be brought about either by warming the drops, or by mixing a non-precipitating drop with one in which precipitation is going on. (Wetzlar.)

Active iron is positive towards platinum in solution of sulphate of copper, and causes deposition of copper on it. Iron rendered passive by ignition decomposes sulphate of copper; iron made passive by nitric acid does not (neither does it decompose nitrate of copper, except when placed in contact with metallic copper. *Herschel*); the latter also gives but a very feeble current with platinum, towards which it is positive. Iron rendered passive by nitric acid becomes coated with copper, and is rendered active by immersing it in sulphate of copper in contact with zinc, cadmium, tin, active iron, or copper,—whereas contact with platinum, gold, or silver produces no effect. (Schönbein.)

Steel wire rendered passive in ammonia or solution of nitrate of silver soon becomes active in sulphate of copper, covering itself with copper in a minute; the latter remains bright for a day in concentrated and somewhat acid nitrate of copper, but instantly acquires a coating of copper when touched with active iron, or with zinc, tin, or lead. If the iron has been washed with water, after immersion in the silver solution, the deposition of copper takes place much more quickly. When an active and a passive iron wire connected by the galvanometer are dipped into an acid solution of nitrate of copper, a strong deflection of the needle is produced, and the passive iron becomes coated with copper. (Wetzlar.)

In a mixture of equal parts of concentrated solution of sulphate of copper and fuming nitric acid, a bar of active iron remains perfectly bright. But if it be scratched below the surface of the liquid with a flint or touched with a similar bar of iron, a deposition of copper takes place upon the bar first immersed, commencing at the point of contact. When the solution is very dilute, the iron at first becomes coated with copper, gas being evolved at the same time,—but recovers its natural brightness after the liquid has been agitated several times. (Schweigger-Seidel, *Schw.* 53, 167.)—Active iron precipitates copper from a mixture of aqueous solution of nitrate of copper with an equal quantity of nitric acid; but if it be first connected with platinum and then immersed, it does not acquire a coating of copper;—even after the removal of the platinum, the deposition of copper does not take place for some time. (Faraday.)

If one end of an iron wire be covered with peroxide of lead (by the decomposition of acetate of lead in the current of the voltaic battery) and this end dipped before the other into a solution of sulphate of copper, no copper is precipitated while both ends are in the solution; but as soon as the covered end is taken out, copper is precipitated on the other; similarly, when the latter is taken out. If an iron wire coated with peroxide of lead, and also an active iron wire, be connected with the galvanometer, and the latter dipped first into the solution, positive electricity passes from the former through the galvanometer to the gins to assume a

coating of copper as soon as its connection with the other wire is broken off.—The cups *a*, *b*, and the siphon *h* (*App.* 2) containing solution of sulphate of copper, if the end *o* of the iron wire covered with peroxide of lead be immersed first, and the active end *p* afterwards, the latter does not become coated with copper; neither does the deposition take place when the siphon *h* is replaced by a wire of iron, copper, or brass; but it is brought about by the introduction of a platinum wire. If the wire *a p* be first immersed, then the active wire *h* dipped, first into *b* and then into *a*, the end in *b* becomes covered with copper, but not that in *a*. When the end *o* covered with peroxide of lead is taken out of the liquid, the end of the wire *h* which dips into *a* also becomes coppered. If *o* remains in *a* and a second iron wire *a* is dipped, first into *a* and then into *b*, the end *g* of the first wire *h* likewise acquires a coating of copper. (Schönbein.)

[When peroxide of lead and iron are placed together in solution of sulphate of copper, the latter takes oxygen and sulphuric acid from the contiguous atoms of the salt, and dissolves. But the separated copper is not precipitated on the iron—but takes, in its turn, oxygen and sulphuric acid from the contiguous atom of sulphate of copper. (*App.* 17.) Thus, the decomposition and recomposition of the atoms of sulphate of copper is continued, in the manner described on page 342, *f*, till it reaches the peroxide of lead. The separated atom of copper lying next to this oxide, robs it of its second atom of oxygen, so that protoxide of copper and protoxide of lead are produced. This change takes place, because peroxide of lead retains oxygen less forcibly than protoxide of copper; and as long as any peroxide of lead remains undecomposed, no deposition of copper can take place on the iron. The iron need not on this account be regarded as passive; for it is constantly taking up oxygen and acid, and dissolving. This oxidation of the iron causes negative electricity to be set free from it;—the peroxide of lead which loses oxygen must take up negative electricity;—hence negative electricity goes from the iron through the galvanometer to the peroxide of lead, or positive electricity in the opposite direction. If, in the above experiment, the two vessels are connected by a siphon, the portions of liquid contained in them act as one liquid, and the process is the same. If the siphon be replaced by a platinum wire, the peroxide can no longer restore by transposition the oxygen which the copper has given up to the iron: for the platinum is placed between the two, and therefore copper is deposited on the iron. But if iron or any other oxidable metal takes the place of the siphon, the process just described goes on in the cup *a*,—that is to say,—oxidation of the iron without deposition of copper, and reduction of peroxide of lead. In this case, negative electricity accumulates in the wire *h*, and positive electricity in the reduced oxide of lead. In accordance with this, the decomposition of the sulphate of copper in the vessel *b* goes on in such a manner, that the end *p* takes up oxygen and acid, and sends the negative electricity thus set free to the oxide of lead; while copper is deposited on the end *i* of the wire *h*, and takes up the negative electricity, which is transferred to this wire from *g*.]

Platinum is positive with peroxide of lead in solution of sulphate of copper, the oxide of lead gradually disappearing. (Schönbein.) [The electric current is due to the decomposition of the peroxide of lead. The nature of this decomposition requires further examination.]

A plate of silver connected with graphite in a solution of nitrate of

copper becomes coated with metallic copper. (Pfaff.) [Did the graphite contain iron?]

Salts of mercury. Iron becomes inactive in subnitrate of mercury (Keir), more passive indeed than in nitric acid,—and is subsequently as passive towards sulphate of copper, as if it were coated with peroxide of lead. (Schönbein.)—In solution of corrosive sublimate, mercury is deposited on silver, gold, or platinum, connected with zinc, tin, lead, iron, or copper.

Silver salts. In solution of nitrate of silver, that metal is precipitated on silver, gold, or platinum, as soon as these metals are connected with tin or copper likewise immersed. (Singer.)

Iron precipitates a very dilute solution of nitrate of silver; it also precipitates a concentrated solution when hot, ochre being formed by the action,—but, at ordinary temperatures, iron does not act on a strong solution of nitrate of silver, whether it be neutral or contain excess of acid.—If, on the other hand, a quantity of silver be dissolved in nitric acid not sufficient to saturate it, so that the free nitric acid remains charged with nitrous acid—or if fuming nitric acid or oil of vitriol be added to a neutral solution—or if a neutral solution be mixed with alcohol and left to stand for some time,—iron will at first precipitate silver from such a solution; but the silver dissolves up again after a time, and leaves the iron in an inactive state.—The liquid poured off from the iron behaves in the same manner with a second piece of iron. Iron which has been rendered inactive, recovers its activity after the removal of the surface, or even after the slightest rubbing; likewise after lying under water for some time (but not under ammonia). It does not dissolve in fuming nitric acid, even after the addition of water.—If iron which has lost its activity be brought in contact with active iron within the liquid, a deposition of silver takes place on the latter—then also on the former; but the silver, subsequently disappears, and both pieces of iron remain inactive. Iron which has been immersed in fuming nitric or a saturated solution of silver, is likewise inactive towards the above solution which contains nitrous acid. Iron will not precipitate copper from a solution of nitrate of copper which has been mixed with nitrate of silver—not even on the addition of acid; so likewise iron which has been rendered inactive by a solution of silver no longer precipitates copper from the sulphate or nitrate. (Keir, *Versuche u. Beobachtungen*, Gött. 1791; abstr. *Schw.* 53, 154.)

When iron nails are mixed with pieces of silver and digested in excess of nitric acid, the silver dissolves, while the iron remains undissolved even after the acid has been boiled. Sometimes the iron is alternately attacked with violence and left in the passive state. (Dumas, *Schw.* 57, 23.)

Iron precipitates sulphate but not nitrate of silver. Seldom only does it happen that after the iron has remained for weeks in a dilute solution of silver, a few shining laminæ or dendrites of silver appear upon it, a corresponding quantity of iron having been dissolved. Iron does not precipitate silver from a mixture of 1 part of concentrated solution of nitrate of silver with 1 part of nitric acid of sp. gr. 1·2; but with 1½ of nitric acid, the iron immediately acquires a coating of silver, which is dark at first, then becomes whiter, and afterwards brilliant; the silver then redissolves with strong evolution of nitric oxide gas, and leaves the iron, bright and whiter than in its ordinary state:—on further addition of acid

the iron likewise remains passive. If the iron be touched for a short time below the surface of the liquid with active iron, it is again attacked and covered with silver,—but subsequently becomes passive again, as the silver dissolves. If the immersed piece of active iron be kept at a little distance from the passive iron, the silver which deposits on the former soon effects metallic communication between the two,—and then the action goes on as just described.—Iron likewise becomes passive in a neutral solution of silver, but not so completely as in an acid solution.—If an iron rod be dipped ten times into a solution of silver, and washed after each immersion, the solution is found to be free from iron at the end of the experiment. —Very gentle wiping with blotting-paper destroys the passivity of an iron rod; but a steel wire remains passive even after rubbing with blotting-paper, or with Paris red and leather,—and even after gentle filing or careful scraping with a steel scraper,—so that the change of state cannot arise from a superficial deposit. (Wetzlar.)—[If only individual spots remain covered with peroxide of iron or graphite, they will, when the iron is again immersed in the silver solution, facilitate the formation of the film of oxide of iron on the exposed parts.]

Iron rendered passive in a dilute solution of nitrate of silver (1 part salt to 12 parts water), then connected with active iron, and dipped into a concentrated solution of nitre, appears strongly negative: the deflection of the galvanometer is however soon reduced to nothing, because the iron recovers its activity. If the iron be taken out of the solution and washed with water, the deflection produced is less than before;—after a second washing, still less;—after the iron has been dried at a gentle heat, it becomes very small indeed, and is sometimes even reversed. Steel retains its active state much longer, sometimes from 8 to 14 days after drying; but in water, it becomes active in half a minute. (Wetzlar.)

In a solution of 1 part of nitrate of silver in 12 parts of water, zinc is first positive towards tin, then negative, then positive, then negative (or at all events less positive), then permanently positive. In a dilute solution, zinc is permanently positive towards tin.—Tin in the above solution (1 : 12) is positive towards lead at first, negative after 13 minutes, then again positive. (Fechner.)

A very dilute solution of silver, even when it contains free acid, is immediately precipitated by iron. In the solution (1 : 12) iron is negative with copper; but the strength of the action increases and diminishes alternately. The silver, as it is deposited on the copper, gradually approaches the bright iron; as soon as it comes in contact with the iron, the current through the galvanometer diminishes, because part of the electricity goes through the silver. When the greater part of the silver-salt in the liquid has been decomposed, and copper-salt formed in its stead, the iron becomes coated with copper, and exhibits a positive reaction stronger than its former negative reaction. The positive state diminishes, however, in intensity, as the coating of copper becomes thicker. In more dilute silver solutions, iron is permanently positive towards copper, and becomes covered with silver,—even when a quantity of concentrated silver-solution is afterwards added, sufficient to restore the above proportion of 1 : 12. On the other hand, iron continues negative for some time in contact with copper in the solution 1 : 12, even when it is considerably diluted with water,—but by degrees becomes positive. When the solution is moderately diluted, the iron is at first negative towards the copper; but afterwards, when it blackens from deposition of silver, it becomes positive. In the solution (1 : 12) iron is positive towards plati-

num, without however precipitating silver; and the current quickly diminishes, because the platinum in the solution continually becomes less negative. When, therefore, the platinum remains for some time in the solution, before it is placed in contact with the iron—whether the iron has been in the solution for the same time, or is then first immersed—the current is much weaker at the beginning. Taking out and cleaning the iron does not strengthen the current; but the same treatment applied to the platinum produces an increase.

In the solution (1 : 12), and in a stronger solution, iron is at first positive towards silver, but soon becomes neutral. If the solution contains a small quantity of free nitric acid, the iron is first positive, then permanently negative. On the further addition of a very large quantity of acid, it remains bright and negative for a while,—then suddenly precipitates silver and becomes positive; then, when the silver disappears, it again becomes bright and negative;—and so on from four to six times in rapid alternation. If the iron, while bright and negative, be taken out of the liquid, it immediately blackens on the surface. (Fechner.)

Platinum is positive towards gold or silver in the neutral solution (1 : 12),—towards gold, likewise, in an acid solution of the same strength. In a dilute solution, the current takes the opposite direction. (Fechner.)

Active iron placed by itself in a dilute and slightly acidulated solution of nitrate of silver, slowly precipitates the silver in solid dendrites; but in contact with passive iron, it precipitates the metal quickly,—first as a black, loose deposit, afterwards in thin shining crystals. The same effect is produced on a bar of passive iron, on which a few active places have been made by rubbing. (Schweigger-Seidel, *Schw.* 53, 167.)

From a neutral or slightly acidulated solution of nitrate of silver, iron precipitates a small quantity of silver, but not till after some days. In the neutral solution, it gives no current with platinum. When the solution is slightly acidulated, the iron appears feebly positive only at the commencement. In a solution so strongly acidulated that silver is deposited on the iron (and afterwards redissolved), the iron remains strongly positive, as long as the deposition of silver continues. When the precipitation ceases and the silver is redissolved, the current also ceases. If the iron be connected by means of the galvanometer with zinc, tin, lead, copper, or mercury, it always appears negative in the silver solution and becomes covered with crystals of silver; for though the film of oxide of iron may be reduced, the silver, when precipitated, acts instead of the passive iron as the negative metal. (Faraday.)

Acetate of silver is completely decomposed by iron, on the application of heat, whether the solution be neutral or acid: it is likewise decomposed in the cold, when mixed with a large excess of acetic acid. But the solution, whether neutral or slightly acidulated, deposits a small quantity of silver in black flakes on particular parts of the iron, while the other parts become covered with gas-bubbles, and the greater part of the silver remains in solution (many pieces of iron remain quite bright). If the bar of iron be filed after it has ceased to precipitate silver, it will again be rendered active for a time. (Wetzlar.)

Copper, whether in its ordinary state, or after it has been dipped in caustic potash and then washed with water, immediately precipitates silver from the nitrate. In its ordinary state, also, it instantly decomposes acetate of silver; but copper, which has been immersed in potash, produces no effect at first on acetate of silver, and exhibits only a few *dark patches* of reduced silver after a quarter of an hour. (Wetzlar.)

Experiments with solutions of Sulphuret of Potassium.—Faraday experimented with the following liquids: 1. *Yellow solution:* prepared by fusing hydrate of potash with its own weight of sulphur, and dissolving the fused mass in water; (contains quinto-sulphuret of potassium mixed with hyposulphite of potash).—2. *Colourless solution:* Aqueous solution of potash saturated with sulphuretted hydrogen; (may be regarded as a compound of sulphuretted hydrogen with protosulphuret of potassium, or as bi-hydrosulphuret of potash).

When two metals are immersed in the yellow solution, the one which takes sulphur from it is positive towards the other. If the former be thereby covered with a film of sulphuret impenetrable to the liquid, but capable of conducting electricity, the direction of the current will be reversed, if the second metal be capable of abstracting sulphur from the liquid: if this be not the case, or if the metallic sulphuret be a non-conductor, the current will cease. (Faraday.)

In the yellow solution, zinc is strongly and permanently positive towards iron, nickel, gold, or platinum,—because the sulphuret of zinc dissolves in the liquid.

Cadmium is strongly positive towards iron, gold, or platinum, and permanently so when the sulphuret of cadmium is loosely deposited; but if the cadmium has been polished with a glass rod, an impenetrable and non-conducting coating of sulphuret of cadmium is formed, and the current ceases.

Tin is positive towards iron, gold, or platinum, for ten minutes only: after that, the current ceases; because the tin becomes covered with an impenetrable, non-conducting crust of sulphuret of tin. (The circuit no longer conducts a thermo-electric current.)

Lead is positive towards nickel, iron, gold, palladium, or platinum, for two minutes only: the current then ceases, on account of the deposition of sulphuret of lead,—which, though it conducts (the circuit conducts a thermo-current), is not permeable to the liquid. The current does not take the opposite direction, because nickel and the other metals do not take sulphur from the liquid.

Bismuth behaves towards the metals just enumerated just as lead does, excepting that the current continues for half an hour. Towards lead also it is positive at first, but neutral after the lapse of two minutes.

Antimony is permanently positive towards platinum,—because the sulphuret of antimony, which is a non-conductor, forms but a loose deposit.

Copper is positive towards nickel, iron, gold, or platinum. The current diminishes without ceasing altogether; because the sulphuret of copper, which is a good conductor, does not form a hard crust, but falls off in scales.

Disulphuret of copper, both natural and artificial, conducts well and is positive towards platinum,—till, by taking sulphur from the liquid, it passes to the state of protosulphuret, and is thus rendered inactive.

Silver is permanently positive towards iron, nickel, gold, palladium, and platinum,—because the non-conducting sulphuret dissolves as fast as it is formed.

Copper is at first positive towards silver, the latter remaining bright; then the current ceases; afterwards the silver becomes positive, and tarnishes,—then again the copper,—and so on alternately, according as the metallic sulphuret, which is being formed, prevents the copper or the silver from taking sulphur from the liquid.

Iron, nickel, gold, palladium, and platinum, not being capable of

abstracting sulphur from the yellow solution, two of these metals placed together in that solution produce no current. For the same reason, no current is generated by sulphuret of bismuth, galena, iron pyrites, copper pyrites, or scale oxide of iron, either with the metals just mentioned or with one another,—although the circuit gives ready passage to a thermo-electric current.

It is only when the yellow solution is very much diluted, that it renders iron positive towards platinum, in consequence of the formation of a very small quantity of sulphuret of iron.

Iron, platinum, &c. are strongly positive towards protoxide of iron (hydrated?), peroxide of manganese, red lead, white lead, yellow oxide of lead, and most of all towards peroxide of lead; for these oxides yield oxygen to the solution. [The metal more or less reduced takes up negative electricity, and sends positive electricity through the galvanometer to the platinum, &c.] Hence, iron rusted by exposure to damp air, or oxidated by nitric acid, then washed with water, potash, and water again,—and even iron apparently bright and clean (since a film of oxide is always formed on it as it dries), is positive towards platinum at the first instant of immersion in the yellow solution. But iron heated in the air till the surface tarnishes, gives no current with platinum.

The colourless solution of bihydrosulphuret of potash gives corresponding results: Lead, bismuth, copper, silver, and disulphuret of copper, are positive towards iron, nickel, gold, or platinum. Silver is positive towards lead. The current between lead and platinum soon diminishes without entirely ceasing; that between bismuth and platinum ceases almost wholly.—Nickel is slightly but permanently positive towards platinum; iron, first negative, then neutral, then positive,—because, at first, the iron-rust forms sulphuret of iron, which is afterwards dissolved.—Thus far Faraday.

Copper is positive towards iron in hydrosulphate of potash. (H. Davy.) —In solution of liver of sulphur, it is positive towards tin, lead, and even zinc. (Marianini.)

Copper is positive towards iron in concentrated solution of liver of sulphur, and blackens immediately,—while the iron is but slightly blackened. When the solution is moderately diluted, the copper is first negative, then positive. On connecting the two plates after they have been immersed in the solution for some time, the copper immediately becomes positive. It will also remain positive, if the iron plate be exposed for some time to the air and then again immersed,—or if it be replaced by a new one; but if the copper plate be exposed to the air [in which case sulphuret of copper may be converted into sulphate], or immersed for a short time in water containing an acid or common salt,—it will, when again immersed in the solution of liver of sulphur, at first exhibit a negative reaction; just as a fresh copper plate is at first negative towards the old iron plate. The current is not reversed by diluting the concentrated solution with such a quantity of water, that clean copper would be negative in the mixture. (Fechner.)

In concentrated solution of liver of sulphur, antimony and bismuth are slightly positive towards iron, and tin towards lead. Silver and copper are strongly positive towards antimony, bismuth, tin, lead, or iron. Copper is positive towards silver. (Fechner.)

Electrical series in hydrosulphate of potash: Zinc, tin, copper, iron, bismuth, silver, platinum, palladium, gold, charcoal. (H. Davy.)

In the yellow solution (1 measure of concentrated solution to 7 mea-

sures of water): zinc, copper, cadmium, tin, silver, lead, antimony, bismuth, nickel, iron.—In the colourless solution (bi-hydrosulphuret of potash): Cadmium, zinc, copper, tin, antimony, silver, lead, bismuth, nickel, iron. (Faraday.)

Experiments with certain fused substances. Zinc gives a strong current with platinum in fused oxide of lead or chlorate of potash; the presence of water is not absolutely necessary. (H. Davy.) Zinc and platinum form powerful circuits in fused carbonate, chlorate, or nitrate of potash. Still more powerful circuits are formed by iron and platinum in the same salts, or in phosphate of soda. (Faraday.)

In fused nitrate of silver, iron oxidates at the same rate and with the same colours as when heated in the air,—no precipitation of silver ensues. Iron and platinum placed together in the fused silver-salt produce either no current at all, or the opposite of what might be expected,—that is to say,—positive electricity goes from the iron, through the galvanometer, to the platinum. This current is thermo-electric. (Faraday.)

Two Metals and one Liquid, which is unequally heated.

The liquid being contained in the bent tube (*App.* 5), into the arms of which the two metallic wires dip, and the portion in one arm only being heated till it boils, the following results are obtained,—according to Faraday.

In dilute sulphuric acid: Hot iron is strongly positive towards cold tin; hot tin still more strongly positive towards cold iron.—Hot iron is feebly positive towards cold lead; hot lead strongly positive towards cold iron.

In dilute nitric acid: Hot tin or lead is positive towards cold iron; hot iron positive towards cold tin or lead.—Lead is always positive towards tin, but hot lead more strongly than cold.

In aqueous solution of potash: Cold tin or cadmium is feebly positive towards hot lead; hot tin or cadmium strongly positive towards cold lead.

In yellow solution of sulphuret of potassium: Cold zinc is positive towards hot cadmium or tin; cold cadmium or tin is positive towards hot zinc.—Cold zinc, tin, or silver is strongly positive towards hot lead; hot zinc, tin, or silver, slightly positive towards cold lead.—Cold tin is feebly positive towards hot silver (which becomes tarnished); hot tin is strongly positive towards cold silver.

The following are results of a different character: Dilute sulphuric acid with copper and silver: If both arms of the tube are cold, or the silver arm cold and the copper arm hot, the deviation amounts to only 1°; but when the silver arm is heated, it rises to 20°, diminishing again as the liquid cools; in this case, the copper is always positive.—Silver is always positive towards platinum in dilute sulphuric acid; but when both arms are cold, the deflection amounts to 4°; when the silver arm is heated, it is 16°; and when this arm is cold, but the platinum arm hot, 30°.—This increase of the current, by heating the part of the liquid in contact with the negative metal, is due to the increased facility with which the current passes from this metal to the liquid. (Faraday.)

Marianini likewise found that the electric current increases, both when the zinc plate is heated before immersion in dilute acid, and also when this plate is kept cold and the copper plate heated.

Quantity of the Electric Current produced by two Metals and one Liquid.

[The greater the number of atoms of the electro-negative element of the liquid taken up by one of the metals in a given time,—and the smaller the amount of purely chemical, and the greater the amount of electro-chemical action (p. 343, *g*)—the greater is the quantity of electricity which passes from one metal to the other. Consequently, the quantity of the electric current is increased by all circumstances, which, (1), accelerate the decomposition of the liquid by the metal; and (2), facilitate the transference of electricity from one metal to the other, and that of the negative electricity from the inactive metal to the liquid,—whilst contrary circumstances produce the opposite effect.]

A zinc wire and a platinum wire each $\frac{1}{18}$ of an inch thick, and immersed $\frac{5}{8}$ of an inch deep in a mixture of one drop of oil of vitriol with 4 ounces of water, produce in 3·2 seconds as great a deflection of the magnetic needle as thirty turns of a powerful electrical machine. (Faraday.)

Equivalent weights of different metals dissolving in the same liquid generate currents of equal quantity but different intensity; *e. g.* zinc produces a more intense current than copper. (De la Rive.)

Nature of the liquid. Since the rapidity of the chemical process varies with the nature of the liquid, it follows that the same pair of metals immersed in different liquids will produce currents differing in quantity.

Zinc and copper produce a stronger current in dilute sulphuric acid than in water or strong oil of vitriol. (Fechner.) [Because the zinc oxidates most quickly in the dilute acid.]

If a mixture of 100 measures of water and 1 measure of oil of vitriol dissolve 1 part of an amalgamated zinc plate joined with a copper plate, the quantity dissolved in the same time by a mixture of 3 measures of oil of vitriol with 100 measures of water will be 1·6; with 6 measures of oil of vitriol, 1·9; with 9 measures, 2·4; with 12 measures, 4·0; with 15 measures, 4·4; with 18 measures, 2·9; with 21 measures, 2·8; and with 24 measures, 2·4 parts. Hence the strongest action is produced by a mixture of 100 measures of water with 15 measures of oil of vitriol, the specific gravity of which is 1·14. This is the case, whether the plates be only half an inch apart or at a greater distance. (Binks.)

A pair of zinc and copper plates immersed in a mixture of 1 measure of oil of vitriol with 80 measures of water gives a deflection of 106°; in a mixture of 1 measure of hydrochloric acid with 40 measures of water, 58°; of 1 measure of nitric acid with 40 measures of water, 106°; of 1 measure of nitric, 1 measure of hydrochloric acid, and 80 measures of water, 59°; and of 1 measure of oil of vitriol, 2 measures of nitric acid, and 160 measures of water, 120°. The last mixture evolves scarcely any hydrogen gas, and does not dissolve half so much zinc in a given time as the first does.

If a zinc and copper pair in distilled water produce a deflection of 1°, the deflection produced by the same pair in sea-water will be 10°; and in the following solutions, all of which contain 1 part of the material to 100 parts of water, the number of degrees of deviation will be as follows: Cyanide of sodium 10·9, hydrocyanic acid 18, ammonia 16·4, soda 32·6, phosphate of potash 44·7, borax 45·3, phosphate of soda 46, tartar emetic 50·7, sulphate of zinc 51·6, chlorate of baryta 63·2, potash 55·7, protochloride of iron 56·5, nitrate of lime 57, acetate of potash 59,

nitrate of baryta 60, protosulphate of iron 62·3, cream of tartar 62·4, sulphate of magnesia 62·6, acetate of soda 64·9, bicarbonate of potash 66·7, chlorate of potash 68·9, carbonate of soda 69·2, benzoic acid 70·7, melanate of ammonia 71·1, sulphate of soda 74·2, benzoate of potash 76·6, nitre 78, sulphate of potash 80, common salt 84·8, alum 85, citric acid 85·7, acetic acid 87, neutral tartrate of potash 92, tartaric acid 98·7, chloride of calcium 110, phosphoric acid 127, flowers of sal-ammoniac containing iron 13·6, oxalate of potash 149, sal-ammoniac 150, acetate of copper 154, hydrochloric acid 164, oxalic acid 179, sulphuric acid 239, sulphate of copper 154, subnitrate of mercury 278, nitrate of silver 298, chloride of gold 307, nitric acid 358, chloride of platinum 418.—Accordingly as one part of the following substances is dissolved in 100 or 1000 parts of water, the deflection produced on the immersion of a pair of zinc and copper plates, is, in the case of sulphate of magnesia, as 24 : 13; of common salt, as 5 : 3; of acid oxalate of potash, as 27 : 11; and of sulphuric acid, as 9 : 4.—If the deflection in pure water be assumed = 1, that in alcohol = 0·323. The addition of salts to the alcohol produces less increase of deflection than the corresponding addition to water would occasion. (Marianini.)

Temperature of the liquid.—A zinc and copper pair in salt-water at 17° C. produces a deflection of 0·2°; at 35°, the deflection amounts to 1·3°; at 48°, to 2·0°; and at 75°, to 4·0°. The deflection decreases gradually, but more and more slowly as the liquid cools. In liquids which excite a copious current even in the cold, the increase on the application of heat is not so considerable [because in this case the chemical action, being already considerable in the cold, is not so much increased by heating]. (Marianini.)

The quantity of hydrogen gas evolved on a plate of copper connected with an amalgamated zinc plate is 1½ times as great at 15·5° as at 11·7°. (Binks.)

Gradual alteration of the liquid.—Chemical action diminishes, in proportion as the activity of the liquid in contact with the positive metal is diminished by saturation. Circumstances which renew the liquid increase the current.

If two metals are placed in the two arms of the U-tube (*App.* 5), and one of them is moved, that one becomes more positive than the other. Thus, cadmium is positive with tin in dilute sulphuric acid; but if we wait till the deflection has diminished, and then move the tin, that metal immediately becomes positive. (Faraday.)

In water, and solutions of sal-ammoniac, common salt, nitre, or sulphate of zinc, the electric current of a zinc and copper pair diminishes quickly and regularly from the beginning of the action; in dilute acids slowly, often not till the acid is nearly saturated,—slowly also in potash. A current which has grown feeble in a saline solution may be revived by wiping the copper surface with a feather [whereby the alkali, &c. accumulated there is removed]. Wiping the zinc plate is less efficacious, and stirring the liquid in the middle does no good whatever. On the contrary, when the current of a zinc and copper pair in oil of vitriol, solution of carbonate of potash, or liver of sulphur, has grown feeble, it is considerably increased by wiping the zinc plate [in oil of vitriol the wiping removes solid sulphate of zinc],—less by wiping the copper. (Rosenschöld.)

Thickness of the intervening liquid. [The nearer the two metals are to one another in the liquid, and the shorter, therefore, the series of

atoms along which transposition must take place, the less will be the amount of purely chemical, and the greater that of electro-chemical action, and the more abundant therefore the current.]

If the deflection produced by a pair of zinc and copper plates in dilute sulphuric acid—the distance between the plates being 21 lines—be assumed = 1, the deflection at 12 lines distance will be 1·3; at 6 lines, 1·7; at 3 lines, 2·1; and at ½ line, 2·6.—The deflection is greater when the plates are parallel than when they are inclined to one another at an angle of 45°;—and least of all when they are perpendicular to each other. (Bigeon.)

According to the distance between the amalgamated zinc plate and the copper plate, and accordingly as 100 measures of water are mixed with 1, 3, 6, 9, or 12 measures of oil of vitriol, the number of seconds required for the evolution of a given quantity of hydrogen gas is as follows:

Distance.	Measures of Oil of Vitriol.				Distance.	Measures of Oil of Vitriol.			
Inches.	1	3	9	12	Inches.	1	3	9	12
½	180	85	60	45	22	640	230	165	145
1	245	135	110	95	24	655	235	161	145
2	370	170	120	120	26	660	265	190	145
4	375	155*	125	125	28	680	295	190	145
6	345*	170	120*	125	30	690	290	190	170
8	400	170	130	125	32	790	300	190	200
10	460	170	130	140	34	805	310	220	210
12	485	185	130	145	36	825	360	220	170
14	515	200	145	145	38	885	365	200*	170
16	530	205	145	145	40	900	370	230	170
18	545	215	165	130*	42	910	370	240	170
20	590	220	165	145	44	920	370	240	170

The law enunciated by Cumming and Ritchie, viz., that the current varies inversely as the square root of the distance between the plates, is not confirmed by these numbers. With the weakest acid (1 measure of oil of vitriol to 100 measures of water) the current at the distance of 44 inches is to that at half an inch as 1 : 5; with the strongest acid (12 measures of oil of vitriol to 100 measures of water) the ratio is as 1 : 3¾. The greatest diminution occurs in all cases at the increase of the distance from ½ inch to 1 inch. The anomalies which occur in the table are marked with a star. (Binks.)

Surface of the positive metal.—A moderately rough amalgamated zinc plate produces the strongest action: when the plate is either quite smooth or very uneven, the action is weaker; in the latter case, too much mercury remains in the hollows and interferes with the action of the acid. —When amalgamated zinc is constantly used, the impurities which it contains accumulate on its surface and weaken the action of the acid; hence it must be cleaned occasionally. (Binks.)—When a plate of amalgamated zinc connected with copper and immersed in dilute sulphuric acid has become covered with bubbles of hydrogen gas, the current is increased in the ratio of 2 : 3 by removing the bubbles by agitation, and thus increasing the effective surface of the zinc. The current is most weakened by placing the zinc plate in the horizontal position, whereby a considerable quantity of gas is suffered to accumulate.

Conducting power of the connecting wire.—[The more the passage of negative electricity from the positive to the negative metal is impeded by imperfect conduction, the more does the electro-chemical action diminish, and the purely chemical action increase.]

If a pair of zinc and copper plates immersed in water be connected at one time by a thick and short wire, at another by a very thin and long wire, which offers 7000 times as much resistance as the former, the quantity of the current in the first place will be to that of the second as $1\frac{1}{9} : 1$; but in dilute sulphuric acid, the ratio = 191 : 1. (Fechner.) [The small quantity of electricity developed by the water finds an easy passage even through the long thin wire,—hence the current is but slightly weakened; but of the large quantity developed by the dilute acid, only a very small portion goes through the thin wire,—hence, in this case, the negative electricity set free in the zinc is, for the most part, transferred directly to the hydrogen.]

When zinc and copper are connected by a very thin copper wire, 16,000 feet long, the quantity of the current produced, varies—accordingly as the metals are immersed in weak or strong nitric acid (the latter of which likewise evolves gas on the copper)—in the ratio of 100 : 52.

The copper wire which connects the two metals gives a stronger current, when its conducting power has been increased by previous ignition. (Binks.)

Nature of the negative metal.—[The previous assumption that the electric current is stronger in proportion as the negative metal employed is more decidedly negative towards the positive metal, *e. g.*,—stronger with silver than with copper, and with platinum than with silver, &c.,—is not found to be correct in all cases, at least as regards *Quantity*. The facility with which negative electricity is transferrod from the negative metal to the separated electro-positive element of the liquid, appears to vary according to the nature, both of the liquid and of the metal.]

Zinc in dilute sulphuric acid produces a stronger current with copper than with platinum, because the latter transfers the negative electricity to the liquid less readily than the former. (De la Rive.)

In dilute sulphuric or nitric acid, and in solution of common salt or caustic potash, zinc gives a stronger current with iron than with any of the other metals, even though they may be much more powerfully negative than iron. (Poggendorff.) Likewise, in solution of nitrate or carbonate of potash, zinc gives a more abundant current with iron than with copper; but in pure water, dilute hydrochloric acid, solution of sulphate of soda, carbonate of ammonia, or sal-ammoniac, and in alcohol, it gives a stronger current with copper than with iron. (Petrina, *Zeitschr. Ph. v. W.* 6, 281.)

Charcoal, though more negative than platinum, gives a weaker current with zinc; it is considerably improved by the precipitation of platinum on its surface. (Smee; *Comp.* Roberts and Poggendorff, p. 350, and Marianini, p. 351.)

Condition of the surface of the negative metal.—[The more uneven the surface of the negative metal, the more abundant is the current. The readier evolution of gas,—*e. g.*, of hydrogen gas—on inequalities of surface (p. 271), must here be taken into account. Covering the surface of the negative metal with thin films of substances having less conducting power weakens the current.]

When the copper connected with the zinc has a smooth surface, the deflection is less than when it is perforated, bent in various ways, engraved in squares, or scratched with a file in all directions. (Bigeon.)

The hydrogen escapes most abundantly at the edges and angles of the negative metal. Unignited platinum or silver does not take up the liquid so readily, and therefore does not give so strong a current as that which

has been ignited. Charcoal long exposed to the air is less effective than freshly ignited charcoal. Spongy platinum, or platinum foil covered with platinum powder, acts more strongly than smooth platinum foil. The following substances immersed in dilute sulphuric acid, in contact with amalgamated zinc, liberate the following quantities of hydrogen gas in a minute: Platinum foil covered with platinum powder, 5 cubic inches; smooth platinum foil, after ignition, 1; the same unignited, $\frac{1}{6}$; platinized coke, $\frac{3}{5}$; common coke, $\frac{14}{25}$ cub. in. If the liquid contains nitric acid, and consequently no gas is evolved, the current is not much increased by the pulverulent condition of the surface: hence it is the more rapid evolution of gas, and not the extension of surface, that causes the increase in the current. Other finely divided metals do not act so powerfully as platinum, with the exception of palladium,—which however does not produce much effect in the spongy state—but when precipitated upon platinum or silver, acts as strongly as finely divided platinum. Considerable effect is produced by platinum precipitated on palladium, silver, or plated copper. The silver or plated copper (the copper surface of the latter being covered with varnish) is immersed in water acidulated with sulphuric acid, to which some solution of chloride of platinum has been added,—and connected by a wire with a zinc plate contained in a porous vessel filled with dilute sulphuric acid, and immersed in the first mentioned fluid. The platinum attaches itself to the silver—provided the surface of this metal has been previously roughened with strong nitric acid—so strongly, that it cannot be removed by rubbing. (Smee.)

Ignition renders a copper plate more active, by increasing its conducting power and removing any impurity—for example, the grease of the finger—which may be attached to it.—A plate of copper thrown in a state of ignition into sulphuric acid, and then cleaned, exhibited remarkable activity.—While the circuit is closed, the copper connected with zinc in dilute sulphuric acid is continually contracting impurities,—in consequence of which, the evolution of gas, and therefore also the electric current, suffers considerable diminution. If the quantity of hydrogen gas evolved on the surface of the copper in the first 5 minutes be 35 measures, the quantity evolved in the second equal interval will be 33 measures; in the third, 29; in the fourth, 24; in the fifth, 17; and in the sixth, 9. On cleaning the copper plate, the quantity again rises to 33 measures. (Binks.)

Relative extent of surface of the negative metal.—[The greater the surface of the negative metal, the greater also is the facility with which the negative electricity passes from it to the separated positive element of the liquid (hydrogen, metals, &c.),—and the stronger therefore is the current.]

The surface of the zinc plate remaining the same, the quantity of the current is considerably increased by enlarging the surface of the copper plate. In dilute sulphuric acid, the current is doubled by increasing the copper surface twofold, trebled by increasing it tenfold, and quadrupled by increasing it thirty-fold. Enlarging the zinc surface, while that of the copper remains the same, produces but little increase of the current [because this relative diminution of the copper surface increases the amount of purely chemical action]. Increased thickness of the metal plates has no effect whatever. (Marianini.)

Increasing the surface of the negative metal strengthens the current most, when the chemical action is weakest. (De la Rive.)

A zinc plate whose surface is equal to $\frac{1}{4}$ of that of the copper plate, gives as strong a current as it would yield [illegible]face were equal to

that of the copper; but if the zinc surface be still further diminished, the current decreases. (Mullins.)

The greater the distance between the two plates, the greater is the increase in the quantity of the current produced by a given enlargement of either of the plates. The distance between the metals being 4 lines in one case and 9 lines in the other, and the deflection produced when the two plates have equal surfaces being assumed = 1, the following are the deflections obtained on increasing the surface of one or other of the plates. (Bigeon, *Ann. Chim. Phys.* 46, 80):

Distance = 4 inches.			Distance = 9 inches.		
Zinc surface.	Copper surface.	Deflection.	Zinc surface.	Copper surface.	Deflection.
1	1	1	1	1	1
2	1	1·13	2	1	1·25
5	1	1·2	3	1	1·3
1	2	1·45	1	1·5	1·21
1	5	2·33	1	2	1·47
			1	2·5	1·66
			1	3	2·28
			1	4	2·69
			1	5	3·00

The greater the surface of the copper, the smaller is the quantity of hydrogen gas which attaches itself in bubbles to the surface of the amalgamated zinc [the smaller is the amount of purely chemical action]. *Binks.*—Several experiments of Binks', on the quantity of hydrogen gas evolved on the copper, according to the extent of copper surface, and likewise according to the distance of the copper plate from the amalgamated zinc plate, will be found in the *Phil. Mag. J.* 12, 171.

Movements of mercury in the simple Galvanic circuit.—When mercury together with another metal comes in contact with different liquids, peculiar motions of the liquid and of substances floating in it are often produced. [The immediate cause is doubtless to be found in motion produced in the mercury itself,—which motion is communicated to the other liquid and is there more easily perceived. But the cause of the original motion in the mercury is yet to be discovered.]

1. Small pieces of potassium or sodium placed on the surface of mercury covered with a thin film of water, move rapidly about, rotating at the same time, until they are oxidated. On dry mercury in dry air, no motion is produced.

Pieces of an alloy of antimony and potassium exhibit similar effects, the smaller ones rotating rapidly, those of greater magnitude revolving in large circles, and oblong pieces of still greater size moving backwards and forwards. The motion continues, till a film of carbonaceous matter and other impurities (previously existing in the alloy) is formed on the surface of the water. A few drops of nitric acid likewise check it in a great degree.

Small pieces of an alloy of bismuth and potassium move about both on mercury covered with water, and likewise—though more slowly—on the naked surface of that metal. In the latter case, the moisture of the air comes into play;—for, on perfectly dry mercury in perfectly dry air, no motion takes place,—though it immediately commences on the addition of water. The motion in common air likewise ceases when the air is removed by the air-pump, but recommences on its readmission. When water is present, however, the motion continues even after the air has been

exhausted. During the motion, a black film, consisting of charcoal, finely divided bismuth, and bubbles of hydrogen gas, is formed on the surface of the water and mercury. This film is pushed aside by the moving pieces of metal. But if a metallic rod of bismuth, zinc, tin, iron, copper, brass, or silver, be dipped, not merely into the water but into the mercury also, the film quickly collects around it—even from a considerable distance—and heaps itself up upon it;—and this process goes on till all the potassium is oxidated. Rods of wood or ivory do not attract the film;—the cause is therefore electrical. If the positive and negative wires of a battery be immersed in the water—in such a manner that neither or only one of them may touch the mercury,—the film collects round the negative wire; whilst by the positive wire, it is alternately attracted and repelled: on bringing the positive near the negative wire, the film is driven away from the latter. A piece of the alloy of the size of a pea will sometimes continue to move for several days.—When the mercury is covered with solution of common salt, the motion is slower. If a metallic rod be then introduced, it fixes the film and keeps the enclosed pieces of metal at rest, as long as it continues immersed. Gas-bubbles are likewise evolved upon it.—Pieces of lead, tin, or iron, containing but small quantities of potassium, and not capable by themselves of decomposing water, move about and rotate on the surface of wet mercury, the motion being quicker as the pieces are smaller.—Alloys of sodium with antimony or bismuth behave like those of potassium.

These motions proceed from the evolution of hydrogen gas; for an alloy of antimony with a large quantity of potassium moves a little when simply placed on the surface of water or alcohol, and always in a direction opposite to that in which the greatest evolution of gas takes place.—Traces of bismuth, tin, lead, copper, and silver, dissolved in mercury, separate on the addition of potassium-amalgam and water,—because an evolution of hydrogen gas takes place on the bismuth, &c. (Serullas, *J. Phys.* 91, 170; 93, 120; *Ann. Chim. Phys.* 34, 192.—*Comp.* Erman, *Gilb.* 28, 353.)

2. A quantity of mercury in a basin is covered to the depth of a line with solution of common salt, a small crystal of sulphate of copper placed upon it, and an iron wire made to dip through the solution into the mercury. The film of metallic chlorides, which had previously formed, immediately splits,—the mercury becomes bright,—and vortical currents are produced, proceeding from the crystal. The crystal moves and turns itself about in various directions,—diminishes in size,—and dissolves much more quickly than it would if the iron were not there; when it is completely dissolved, the motion ceases. When the crystal touches the mercury, it moves about the surface in circles in a very curious manner. Zinc, bismuth, lead, and copper, act like iron; antimony, silver, gold, and platinum, on the contrary, produce no effect. When the mercury has been used several times for this experiment, and thereby becomes loaded with copper, the motion is produced without the assistance of iron; and in the same manner, copper-amalgam will also produce it without iron.—Mercury placed in contact with iron and solution of common salt, also gives rise to currents in the solution, without the assistance of sulphate of copper,—but this motion is very different from that just described.—If the mercury be placed in a copper vessel lined with blotting-paper, the motion is produced, as soon as the copper and mercury are connected by a platinum wire.

Sal-ammoniac, chloride of potas[illegible]ide of aluminum, sesqui-

chloride of chromium, and protochloride of iron, act much less strongly than common salt; chloride of barium and chloride of calcium act only in the dilute state, and for the most part but feebly. No action is produced by perchloride of iron, chloride of copper, protochloride of mercury, or chloride of platinum; or by chlorate of potash, iodide of potassium, salts of sulphuric or nitric acid, concentrated hydrochloric acid, aqueous solution of tartaric or oxalic acid. In dilute sulphuric acid, the crystal moves at first, but soon becomes covered with a red coating of copper, and is brought to rest. Dilute nitric acid produces motion, merely with mercury and iron; but the addition of sulphate of copper greatly increases the effect. Sulphate of copper may be replaced by pieces of chloride, nitrate, or acetate of copper; with the first of these salts, however, the motion is ill defined, because the solution is too rapid,—and with the last, because it is too slow. Borate and phosphate of copper act only on the addition of nitric acid to the solution of common salt. Salts of bismuth substituted for sulphate of copper produce a slight motion; salts of tin, a stronger one; salts of zinc, lead, manganese, and iron, none at all. Nitrate of silver produces rapid motion, if dilute nitric acid be substituted for solution of common salt. (Runge, *Pogg.* 8, 106.)

Mercury containing a small quantity of zinc in solution acts powerfully with solution of common salt and solid sulphate of copper without iron,—or with solution of corrosive sublimate and solid corrosive sublimate or sulphate of copper. (Poggendorff, *Pogg.* 8, 112).—The addition of hydrochloric or sulphuric acid to the solution of common salt, accelerates the motion of the sulphate of copper. Again, if, in place of the crystal, a drop of solution of sulphate of copper be added to the solution of common salt, the mercury acquires a trembling motion, which is communicated to any light particles that may be floating in the upper liquid. (Gm.)

3. When a drop of a mixture of ordinary nitric acid with an equal quantity of water is placed upon mercury, it spreads itself over the surface. On dipping an iron wire into the mercury, the acid instantly collects round it, while a jerking motion is communicated to the mercury; on withdrawing the wire, the acid again diffuses itself over the surface. This phenomenon is not exhibited by hydrochloric or sulphuric acid. A globule of mercury, four lines in diameter, completely covered with nitric acid, acquires, on the immersion of an iron wire, a violently tremulous, and often a regular rotatory motion,—which is likewise communicated to the iron wire, if it be laid in the proper direction. The motion of the mercury continues for a considerable time, the wire being at the same time strongly attacked;—and as the mercury comes to rest, the acid—which gradually assumes a greenish brown tint—is thrown into a state of violent rotatory motion; at the same time a film collects round the wire, the rest of the mercury remaining bright; and when the wire is withdrawn, the film spreads itself over the entire surface. Zinc and cadmium cannot be substituted for the iron,—probably because they amalgamate too quickly.—The U-tube (*App.* 4) containing mercury, and nitric acid being put into the arm *b* above the mercury,—also an iron wire being made to dip into the mercury in *a* and another into the acid in *b*,—the mercury in *b* falls half a line, whenever the projecting ends of the wires are made to touch one another; bubbles of gas are formed on the surface of the mercury, and move to and fro every time the circuit is opened and closed; and above the mercury, there is formed a greenish brown solution of iron (protonitrate of iron containing nitric oxide), which is driven to the top when the circuit is

closed. When solution of the iron ultimately takes place, attended with evolution of gas, the peculiar phenomena disappear. (Runge, *Pogg.* 15, 95.)

4. If a globule of mercury at the bottom of a solution of subnitrate of mercury (which had better consist of 1 measure of a solution of sp. gr. 1·28 prepared in the cold, and containing no more free acid than is necessary, diluted with 2 measures of water) be touched with a strip of zinc, the mercury will run up the zinc with great rapidity, then fall down again, and so on,—at the same time producing currents in the solution, either till all the zinc is destroyed, or the mercurial solution exhausted.—If a strip of zinc 3 lines long be laid on a globule of mercury from 1 to $1\frac{1}{2}$ line in diameter, contained in a small saucer, under a solution of subnitrate of mercury,—the mercury, as soon as it has wetted the zinc, begins to move by fits and starts—is violently thrown to and fro—and presently acquires a rotatory motion, running round a circle $\frac{3}{4}$ of an inch in diameter at least thirty times in a minute. When all the mercurial solution is decomposed, or a sufficient quantity of zinc is dissolved in the mercury, the motion suddenly stops. Other metals, *e. g.* iron, do not produce this effect.—The motion stops as soon as the mercury has dissolved $\frac{1}{100}$ zinc; it may therefore be immediately stopped by adding a little zinc-amalgam to the mercury. The rotation appears then to depend on the formation of an amalgam of zinc, and to cease as soon as this substance is formed. (Runge, *Pogg.* 16, 304; 17, 437.)

2. *One Metal and one Liquid.*

a. When only one piece of Metal comes in contact with the Liquid.

When dilute sulphuric or nitric acid is poured upon iron filings, giving rise to the evolution of hydrogen or nitric oxide gas, negative electricity appears in the residue. (Lavoisier & Laplace, *Crell. Ann.* 1788, 1, 351.)—When an acid is dropped on an oxidable metal in a state of ignition, the metal becomes negative, while the vapour exhibits positive electricity. (De la Rive.)—When pulverized nitrate of copper is wrapped up in tinfoil, decomposition ensues, attended with emission of sparks and evolution of gas,—and negative electricity appears in the resulting product. (R. Böttger.)

[Metals during oxidation give out negative electricity, which must be taken up by the hydrogen or nitric oxide gas evolved. But, in consequence of the rapid evolution of gas, this transference of electricity is not complete; the gases, therefore, take the required quantity of negative electricity from the electricity which is in the latent state; and hence they appear positively electrified, whilst negative electricity appears in the residue.]

b. When two pieces of the same Metal dip into one Liquid.

The two pieces of metal being connected by a galvanometer, a feeble current is produced, in those cases only when some difference exists in the physical character or in the surface of the pieces of metal, or in the temperature or composition of the liquid in different parts.

Different physical constitution of the pieces of metal.—Soft copper, iron

or zinc in dilute sulphuric acid is negative towards the same metal hardened as much as possible by hammering. Soft steel, on the contrary, is positive towards hard steel. (Ritchie.)—Spongy platinum in dilute sulphuric or nitric acid is negative towards platinum wire. (De la Rive.)

Different magnitude and smoothness of surface.—If a small piece of zinc foil, and another piece twenty-four times as large, are immersed in cold dilute acid, the former is positive; but in stronger acid, especially when heated, the larger piece is positive. (Vliet & Haaxmann, *N. Br. Archiv.* 3, 131.)

If the surface of a zinc plate be increased twofold by cutting into it with a file, this plate will be strongly negative in nitric acid towards another of the same size, but having a smooth surface,—although the rough plate will be most rapidly oxidated. (Ritchie, *N. Edinb. J. of Sc.* 2, 150.)

In water containing but a small quantity of sulphuric or nitric acid, a large zinc plate is negative towards a small one. With a larger quantity of acid, and particularly when the liquid is heated, the current goes the contrary way. (Oerstedt.)

Whether the plates are equal or unequal in size, they give, when simultaneously immersed in acidulated water, either a feeble current which soon ceases, or no current at all. In dilute, as well as in moderately strong sulphuric acid, the narrower zinc plate is almost always negative,—rarely positive. The current appears to be produced only when the two plates are not immersed exactly at the same time. (Wetzlar.)—Walcker also did not obtain any satisfactory results with plates of different sizes, and having surfaces of different degrees of smoothness.

[Compare Zamboni's piles with two elements.]

Difference in cleanliness of surface.—Copper covered with oxide is negative, in solution of nitre, towards clean copper. (Becquerel.)—In dilute sulphuric acid,—zinc, tin, lead, iron and copper, oxidated on the surface, are negative towards the same metals with bright surfaces. (Marianini.)—Zinc, tin, iron, or copper, after being heated in the air till it tarnishes, is negative towards bright metal, in acid, alkaline, or saline liquids. (H. Davy.)—In hydrosulphate of potash, copper covered with sulphuret is negative towards clean copper, but positive towards the same metal heated in the air till it has become tarnished. (H. Davy.)—Tin which has become dull by immersion in nitric acid, is negative in solution of potash towards clean tin,—but exhibits a positive reaction after the latter has also become dull. (H. Davy.)

In dilute sulphuric acid or sulphate of soda, copper wire, previously immersed in solution of blue vitriol, is negative towards ordinary copper wire. So likewise is copper wire which has been immersed in nitrate of copper, towards ordinary copper in nitric acid. In hydrochloric acid, platinum wire covered with chloride of platinum, is negative towards the same wire in its ordinary state. (Walcker.) [In these cases, the combination of the enveloping liquid with the second liquid must also be taken into consideration.]

Different times of immersion.—When two equal pieces of the same metal are immersed in one of the following concentrated solutions, *the piece first immersed,* is, according to Yelin, positive or negative,—and produces various degrees of deflection, as indicated by the signs and numbers in the following table.

	Zn.	Sn.	Pb.	Fe.	Sb.	Bi.	Cu.	Brass.	Ag.	Au.	Pt.
Phosphoric acid	+10	− 2½	+ 2	+ 2½	+ 2½	−1½	− 1½	− 2½	+ ½	+ ½	+ 1
Sulphuric „	−15	− 2	+ 6	+ 5	+ 1	−2	−20	− 1½	+ 8	+ 1½	+ 1
Hydrochloric „	+30	− 5	+ 2½	+17	−15	+3	−15	+10	+10	+ 2½	+ 1
Nitric „	−54	−10	−50	−90	−20	−4	− 8	−10	+15	−20	+ 5
Tartaric „	+ 5	+ 1	+ 1	+ 3½	+	+	+	+ 1	+ 1	+	+
Acetic „	+ ½	+ ½	+ ½	+ 2	+	+	−	+	+ 1	+	+
Ammonia	+ 1½	− 1	− 1	− ½	+ 1	+1	+ ½	+ 1	+ 2½	+ 1½	+ 1
Potash	+40	+ 5	+ 2	− ½	+ 1	+1½	− 2	+ 1½	+ ½	+ ½	+10
Soda	+10	+ 5	+ 0	+	+ 5	−2	+10	+ 2½	+ ½	+ 1	+ ½
Sal-ammoniac..	+ 5	+ ½	+ 2½	+ 3	+ 1	− ¾	+ 1½	+ 5	+28	+ ½	+
Common salt ..	+ 2	+	+ 1	+ 1	+ 2	−	−	−	+ 6	+ 1	+
Alum	+ 3	+ ½	+ 1	+ 4	−	− ½	+ ½	− 1	+ 8	+ 1	+

In another experiment of Yelin's, the platinum or silver first immersed in sulphuric acid, was negative. [Many accidental circumstances may have influenced the results of the foregoing table: it is remarkable that the actions in potash and soda often exhibit opposite characters. The negative reaction of the piece first immersed in sulphuric acid is, however, constant.]

If two pieces of zinc are successively immersed in hydrochloric acid, the piece first immersed—which is positive—retains this character, even when both pieces are taken out and then put in again in the reverse order. (Yelin.)

Of two pieces of zinc, tin, iron, or copper, the one first immersed in dilute acids, alkalis, or saline solutions, is negative towards the other; because a film of oxide collects upon it [?]: in concentrated solution of potash, also, the first-immersed piece of zinc or tin is negative. (H. Davy.)

The first-immersed piece of zinc is positive towards the other in a mixture of 1 part of oil of vitriol and 100 parts of water (Marianini); also in a mixture of 1 part oil of vitriol, 1 part nitric acid, and 50 parts water (Oerstedt); in oil of vitriol, on the contrary, it is negative (Wetzlar), but the current soon ceases. (Buff.)—Similar relations are exhibited by lead. —When plates of zinc, tin, lead, or iron, are left in oil of vitriol in contact with platinum, till the current has reached its minimum,—they exhibit a negative reaction towards a plate of platinum subsequently put in connection with them. (Buff.)

If a zinc (tin, or copper) plate be left for some time in water acidulated with sulphuric acid, another for an equal time in solution of common salt, and both plates subsequently immersed in solution of salt, the first will be positive towards the second. (Marianini.) [Some acid may remain attached to the first.]

The first-immersed zinc plate is positive towards the last in dilute sulphuric acid, negative in solution of ammonia, negative also in dilute nitric acid,—the more strongly in proportion to the length of time for which it is immersed before the other;—and the plate which was first immersed in nitric acid [covered with oxide, therefore] is found to be negative towards the one which was immersed last, when both plates are plunged into dilute sulphuric acid or salt water. (Marianini.)

If a piece of tin or iron be immersed in oil of vitriol for a short time only, it exhibits a positive reaction towards a piece afterwards introduced; but if the first piece remains in the acid till [from the formation of a crust of sulphate] the evolution of gas ceases, it is found to be negative towards a piece subsequently immersed. (Buff.)

Two wires of tin, lead, iron, or copper, dipped at the same time into hydrosulphate of potash, produce no current: but the one first immersed is negative; because it becomes covered with metallic sulphuret,—in consequence of which it exhibits a negative reaction towards clean wire in other

liquids.—In the case of silver or palladium, on the contrary, the piece first immersed is positive, because sulphuret of silver (or sulphuret of palladium) is more positive than the pure metal. (H. Davy.)

Of two plates of lead or iron immersed in concentrated nitric acid, the one first immersed is negative towards the other. (Marianini.)

In nitrate of silver, the first immersed plate of iron is very weakly negative. (Fechner.)

The plate of brass or copper first immersed in nitric acid, the plate of copper first immersed in ammonia, and the plate of platinum first immersed in aqua regia, is positive towards the one last immersed. (Becquerel.)

In the yellow solution of sulphuret of potassium, first one and then the other piece of copper or silver is positive; and at the moment of change, a film of sulphuret forms on the one which becomes positive.—The electric states of two pieces of silver immersed in hydrochloric acid likewise experience sudden changes. (Faraday.)

When two plates of gold are successively immersed in nitric acid containing a little hydrochloric acid, the one first immersed is negative. So likewise with platinum, exceptig that the current is stronger. (If then, gold be immersed first, and platinum afterwards, in aqua regia, the gold will be less positive than when it is immersed last.) *Marianini.*

The first immersed plate of platinum is positive towards the second in sulphuric acid, hydrochloric acid, nitric acid, aqueous solution of potash, solution of common salt, spring water, or acetate of lead: on the contrary, it is positive in sulphurous acid, sulphate of copper, nitrate of silver, and solution of liver of sulphur. (Fechner.)

[The causes of the electric current produced on the successive immersion of two pieces of the same metal may be the following. (1.) The piece of metal first immersed is freed by the action of an acid from a film of oxide, and thus rendered more positive. (2.) Its surface is roughened,—and thereby, both the action of the acid, and possibly also the direct passage of the negative electricity to the electro-positive element of the liquid, facilitated. (3.) Negative electricity accumulates in the piece first immersed,—and thereby an electric current is excited in the direction, which makes it appear positive. (4.) The piece first immersed may become coated with foreign substances (iron and tin in nitric acid with oxide, zinc or lead in oil of vitriol with a metallic salt, copper in sulphuret of potassium with sulphuret of copper), which weaken the action, and thus render the metal negative.]

Motion.—If two pieces of tin immersed in dilute nitric acid give no current, or if the one last immersed is positive, the other may be made positive by agitating the liquid. With hydrochloric acid the action is weaker. (Faraday.)

Rubbing one of the pieces of metal always makes it positive, even when all rise of temperature is avoided. (Walcker.)

[The motion may free the metal from adhering oxide, or from liquid partly saturated.]

When two platinum wires are immersed in a mixture of 1 part hyponitric acid and 1 part water, and the current at first excited entirely ceases after a few seconds, either of the wires may be rendered negative by taking it out of the liquid for a second and dipping it in again. (Faraday.) [The acid takes up oxygen when exposed to the air; and the current is probably due to the mixture of the acid thus altered with the rest of the liquid.]

Difference of temperature.—If an iron cylinder heated at the lower end, and also a cold iron cylinder, are immersed in water, the cold cylinder becomes positive. (Ritchie.)

If two wires of the same metal are made to dip into a curved tube (*App.* 5), in one arm of which the liquid has previously been heated, and both are kept moving at the same rate (for otherwise the metal most quickly moved would always be positive; and if both were kept still, the heated side of the liquid would alone be agitated by the boiling), the following results are obtained,—according to Faraday:

In dilute sulphuric acid (1 part oil of vitriol to 80 parts water)—zinc, cadmium, tin, lead, or iron, in the heated arm, is strongly and uninterruptedly positive; but after some time, hot zinc and copper become slightly, and hot cadmium more strongly, negative.

In dilute hydrochloric acid (1 measure of acid to 29 of water), hot zinc, cadmium, tin, lead, or iron, is strongly positive.

In dilute nitric acid (1 measure of acid to 50 of water), hot iron is still more strongly positive than in dilute sulphuric acid; hot zinc, copper, and silver are very feebly positive, and only at the first instant. Hot cadmium is at first slightly negative, afterwards slightly positive, then almost neutral. With lead, no current is produced at first; subsequently, the hot piece becomes negative, and remains so.

In concentrated nitric acid, hot iron (which at the same time causes an evolution of gas; *Gm.*) is positive; both ends become passive.

In solution of potash,—hot zinc, cadmium, tin, iron, or copper, is strongly and uninterruptedly positive: a quantity of protoxide is gradually formed on the iron, diffuses itself through the liquid, and passes to the state of peroxide. Hot lead likewise appears positive, but with a sudden start, as if it were negative at the first moment of immersion.

In sulphuret of potassium, concentrated or diluted, hot iron, copper, or silver, is positive. A film of sulphuret forms chiefly on the hot metal, and thus diminishes the action. Zinc and cadmium give no current at first; afterwards, the hot piece becomes strongly negative. Hot lead and tin are slightly negative.

With some exceptions—due, perhaps, to pure chemical action—the hotter metal is positive, because the strongest action is exerted upon it.

Metals which are not acted upon by a liquid, produce—when immersed in a portion of that liquid unequally heated—either no currents or very feeble ones,—probably of a thermo-electric nature for the most part. No currents are produced by gold, platinum, or silver, in dilute sulphuric acid, or by platinum in dilute hydrochloric acid. In strong hydrochloric acid, hot platinum is very feebly negative. In dilute nitric acid, platinum gives no current, palladium and gold scarcely any. In yellow concentrated nitric acid, hot platinum is negative, producing a deflection of 2°; in the orange-coloured acid, it is also negative, the deflection being 10°. In strong solution of potash,—hot silver, gold, and platinum are slightly positive. In solution of sulphuret of potassium, hot platinum is negative; palladium gives no current. (Faraday.)

3. *Two Metals touching one another with two Liquids touching one another.*

In these experiments, the apparatus (*App.* 2, 3, 4, 5, 6, 7,) described (p. 329) are used. One of the metals with one of the liquids may be enclosed in a bladder or a vessel of unglazed earthenware, and this immersed in the other liquid containing the other metal.

a. The two Liquids are of the same Nature, but of different degrees of Concentration.

Faraday's Experiments: *Sulphuric acid.* Cadmium, in oil of vitriol or dilute sulphuric acid, is positive towards tin and iron in the same acid, dilute or concentrated. Tin also is in both cases positive towards iron; iron towards copper and silver, and copper towards silver, but in different degrees. Iron also, when immersed in weak acid, is much more strongly positive towards silver immersed in oil of vitriol, than iron in strong, towards silver in weak acid. On the other hand, zinc, tin, and lead are most strongly positive towards silver, when they are immersed in oil of vitriol.

Nitric acid. Zinc in strong acid is slightly positive towards copper or silver in weak acid; zinc in weak acid is highly positive towards cadmium, tin, iron, copper, or silver in strong acid. So likewise cadmium in weak acid is strongly positive towards tin, lead, iron, copper, and silver, and moderately towards zinc. Tin in dilute acid is positive towards zinc, lead, iron, copper, and silver,—and neutral, or feebly positive, towards cadmium. Lead in dilute acid is positive towards zinc, cadmium, tin, iron, copper, and silver.—Iron in weak acid is positive towards zinc, cadmium, tin, lead, copper, and silver.—Copper in weak acid is positive towards tin, lead, iron, and silver, and slightly so towards cadmium.—Silver in dilute acid is positive towards lead, iron, and copper, and feebly positive towards zinc and cadmium. [The concentrated acid renders the otherwise positive metals negative, by covering them with a film of oxide or nitrate.]

Solution of potash. Zinc is positive towards cadmium, tin, and lead, whether it be immersed in the strong or in the weak solution: so likewise tin is positive towards cadmium, and cadmium towards lead,—but most strongly when the cadmium is placed in the stronger solution.

The strong electric currents here spoken of do not arise from the contact of the two liquids: for when a couple of platinum wires are immersed, the current is scarcely perceptible. (Faraday.)

b. The two Liquids are of different Natures.

The liquid which touches the negative metal is an alkali.—When zinc is placed in dilute acid, and platinum in strong solution of potash, the zinc becomes positive—but much less strongly than when the zinc is placed in the potash and the platinum in the acid.—Tin introduced into this circuit in place of platinum becomes positive even towards the zinc. (H. Davy, Faraday.) Similarly, lead becomes positive towards tin when the former is immersed in potash, the latter in dilute sulphuric acid; the metal in the acid remains bright, that in the potash is attacked. (Faraday.)

Zinc in solution of nitre, and platinum in solution of potash, produce a strong current, capable of decomposing iodide of potassium, chloride of tin, and sulphate of soda. (Faraday.) [The oxide of zinc, as it forms, takes up the potash of the nitre; and the nitric acid is carried by transposition to the free potash.]

The liquid in contact with the negative metal is sea-water.—If the cup *b* (*App.* 2) contains sea-water and copper, while *a* contains sea-water and iron, the cups being connected by a bundle of threads, and potash being gradually added to the sea-water in *a*, the following effects are ob-

served: When a small quantity of potash is present, a little of the iron dissolves, and the copper is completely protected; when the quantity of potash becomes greater, neither iron nor copper is dissolved; and with a still greater quantity of potash, the copper becomes positive and dissolves, the iron does not. (H. Davy.)

The liquid in contact with the negative metal is dilute acid.—When zinc is placed in aqueous solution of potash, and copper in dilute acid, a very strong current is produced. (H. Davy, Berzelius, Walcker.) A feebler current is excited when a neutral compound of the acid and alkali is interposed between the zinc and copper, and the feeblest of all when the arrangement is—zinc, acid, alkali, copper. This arrangement of substances always arises in the course of the action of a galvanic circuit; and consequently the current is constantly diminishing. (Berzelius.)—When zinc is immersed in water,—and lead, iron, copper, or brass, in dilute sulphuric acid,—the zinc is positive.—So likewise, lead immersed in water is positive towards iron, copper, or brass, in dilute sulphuric acid. Nevertheless, the metals immersed in the acid are always the most strongly attacked.—If zinc is immersed in dilute sulphuric acid (1 oil of vitriol to 6 water), and platinum in water,—or the contrary,—the zinc is always positive, and produces the same deflection,—although it is much more strongly attacked in the acid than in the water. Similarly, zinc is positive towards silver, and gives the same deflection, whether the zinc is immersed in water and the silver in dilute nitric acid, or the contrary. The same takes place with zinc and iron, or graphite. (Marianini.) [The feeble current which zinc produces in water easily brings about a transposition of atoms in the acid liquid; the strong current which zinc might excite when immersed in dilute acid, is for the most part arrested in water, —and the violent action between the zinc and acid becomes in great part purely chemical.]

Zinc in a solution of potash or chloride of calcium (Berzelius), or in pure water (De la Rive), is positive towards copper in nitric acid, although the latter is the most strongly attacked. As long as the zinc immersed in potash or chloride of calcium is not connected with the copper, a brisk effervescence takes place on the surface of the latter, the zinc remaining clean. But when the circuit is completed, the zinc immediately becomes tarnished; the evolution of gas at the surface of the copper ceases; and the copper previously dissolved is precipitated on it. Such, at least, is the case when several pairs of these metals are united together. (Berzelius, De la Rive.) [The greater affinity of zinc for oxygen gives rise—as the zinc is connected with the copper—to a transposition of atoms in the two liquids: the oxygen and acid go to the zinc; the alkali and hydrogen, together with copper previously dissolved, to the copper.]

When hard and soft copper are immersed in water, the former is positive (p. 385); but if a little sulphuric, nitric, or hydrochloric acid be introduced into the water containing the hard copper, the deflection immediately increases: on the other hand, the addition of a little hyponitric acid causes it to diminish; and when a larger quantity is added, the current is reversed. (Ritchie.)

The liquid in contact with the negative metal is oil of vitriol. When zinc is immersed in concentrated nitric acid, and copper in oil of vitriol (*App.* 4), the copper is strongly positive; *i. e.*, (according to De la Rive) positive electricity goes from the zinc through the galvanometer to the copper,—which circumstance is attributed by De la Rive to the difficulty which the positive electricity finds in passing from the oil of vitriol to the

metal. According to Marianini, on the contrary, the zinc is strongly positive.

The liquid in contact with the negative metal is strong nitric acid.—Zinc being immersed in oil of vitriol, and copper in strong nitric acid, (*App.* 4) the zinc is positive, though the copper is most strongly attacked. The current is however not so strong as when the zinc is placed in nitric acid and the copper in oil of vitriol: (see above). De la Rive.

If an outer vessel contains strong nitric acid—or a mixture of equal parts of strong nitric acid and oil of vitriol, which works equally well,—and if in this liquid there is immersed a plate of platinum, and a vessel of porous earthenware containing an amalgamated zinc plate and filled with one of the following liquids—which are enumerated in the inverse order of the strength of their action (dilute hydrofluoric acid, hydrochloric acid, sulphuric acid, phosphoric acid, solution of potash—which however stops up the pores of the earthen vessel with crystallized nitrate of potash—soda, common salt, nitre, chlorate of potash, iodide of potassium, spring water, rain water, distilled water),—a very powerful electric current is produced. The dilute hydrochloric acid consists of 1 part of concentrated acid and from 2 to 2½ parts of water; the dilute sulphuric acid, of 1 part oil of vitriol and from 4 to 5 parts water. When the circuit is closed, the nitric acid turns, first yellow, then green, then blue,—afterwards becomes colourless and evolves nitric oxide—and finally, hydrogen gas at the surface of the platinum plate. The dissolved zinc remains almost wholly outside the vessel containing the nitric acid. When the circuit is kept closed for a long time, the liquids become very hot. The nitric acid must be highly concentrated, and renewed as soon as hydrogen gas makes its appearance at the platinum surface.—When zinc is in contact only with dilute sulphuric acid and platinum, it has to overcome the great affinity of oxygen for hydrogen; but when nitric acid is present, the hydrogen separated from the water is carried over by transposition to the nitric acid—combines with part of the oxygen of that substance—and liberates nitric oxide. Hence, in this case, the combination of the zinc with the oxygen of the water is opposed only by the much smaller affinity of nitric oxide for oxygen,—and consequently the solution of the zinc goes on much more quickly, and the electric current is proportionately stronger. (Grove.) [If the nitric acid were in immediate contact with the zinc, the greater part of the negative electricity would be lost, in consequence of the purely chemical action thereby produced; with amalgamated zinc in dilute sulphuric acid, on the contrary, no purely chemical action takes place, the action being entirely electro-chemical, (p. 349)].

If the outer vessel contains an amalgamated zinc plate immersed in dilute sulphuric acid, and a tube of gypsum dipping into it is filled with nitric acid of 1·5 sp. gr. with a piece of iron immersed in it, a current is produced strong enough to decompose water. But as soon as, in the course of the experiment, the nitric acid has attained a certain degree of dilution, the passive iron dissolves with violent effervescence. The wire outside the acid suffers still more from the nitrous vapours; hence it must be coated with wax. If iron instead of zinc is immersed in the dilute sulphuric acid, the action is the same, but continues for a shorter time; and the passive iron in the nitric acid dissolves more quickly. The addition of nitrate of mercury to the nitric acid retards the solution of the iron in the nitric acid for a somewhat longer time; but this salt crystallizes in the gypsum tube and cracks it. (Hawkins, *Phil. Mag. J.* 16, 115.—Grüel's Apparatus, *Pogg.* 51, 381.)

When zinc is placed in a mixture of 1 part oil of vitriol and 6 parts water, and platinumin moderately strong nitric acid,—the circuit produces an electro-magnetization of iron, a hundred times as strong as that produced by a zinc and copper pair of the same size, simply immersed in dilute sulphuric acid. The action gradually increases as the sulphuric acid becomes saturated with zinc, and is remarkably increased by the use of a solution of sulphate of zinc in place of dilute sulphuric acid. [As the zinc takes oxygen and acid from the adjacent atoms of sulphate of zinc, the zinc-atom set free by transposition at the end of the series, likewise takes oxygen and acid from the nitric acid; an indirect action of nitric acid upon zinc is therefore brought about by the sulphate of zinc.] The action of the circuit remains perfectly uniform for three hours; no gas is evolved on the zinc, and scarcely any on the platinum,—because the nitric oxide remains dissolved in the nitric acid and colours it green. A simple circuit of this kind decomposes water feebly; a combination of two such circuits, rapidly. (Pfaff.)

Solution of common salt in place of sulphuric acid is particularly effective in this apparatus. If weaker nitric acid, of sp. gr. 1·19, be used in connection with dilute sulphuric acid, a large quantity of gas is evolved from the nitric acid,—and then the current is much weaker. (Poggendorff.)

If a compact carbonaceous mass be formed by strongly igniting a mixture of pounded coal and coke—a cell formed out of it, and filled with quartz-sand and strong nitric acid—and the whole placed in a vessel containing dilute sulphuric acid, and a plate of zinc 4 inches long and 3 inches wide,—bright sparks are emitted on closing the circuit; fine platinum wire becomes red hot; iron wire, No. 8, burns; and hydrochloric acid, iodide of potassium, lead, and silver salts, are decomposed by the current. (Bunsen, *Ann. Pharm.* 38, 311.) [The nitric acid which oozes through the pores of the coke perhaps also forms a film on the outside of it.]

A circuit of copper, dilute sulphuric acid, nitric acid, and platinum, produces a current nearly half as strong as that which is excited when zinc is used instead of copper. (Poggendorff, *Pogg.* 54, 358.)

If the bowl of a common tobacco-pipe be filled with nitric acid, and placed in a vessel containing hydrochloric acid, a couple of gold leaves simply immersed in the latter will not be dissolved: but on connecting one of them with a platinum wire, the other end of which dips into the nitric acid, the gold leaf thus attached will dissolve, while the other will not. (Grove.) [The gold leaf attached to the platinum takes chlorine from the hydrochloric acid, the hydrogen of that compound passing over by galvanic transposition to the oxygen of the nitric acid.]

The negative metal is in contact with arsenious acid or arseniate of potash.—Tube *a* (*App.* 7) containing solution of arsenious acid with a copper wire immersed in it, and the vessel *b* containing solution of sal-ammoniac with zinc—a black film of arsenic makes its appearance in the course of five hours on the surface of the copper, and afterwards assumes a steel-grey colour and metallic lustre—the change commencing from a single point, and gradually extending over the whole surface. When hydrochloric acid is mixed with the arsenious acid, the copper becomes covered at the surface of contact of the liquid and the air, with white metallic arsenic. If the solution of arsenious acid contains a small quantity of nitric acid, a deposit of white metallic arsenic is formed, principally on the part of the copper which or a liquid—the arsenic being perhaps carried out if arsenin-

retted hydrogen and then precipitated on the wire. (Simon, *N. Fr.* 22, 1, 14.)

When the tube *a* (*App.* 7) contains solution of arseniate of potash with a platinum wire immersed in it, and the vessel *b* contains solution of arsenic with a piece of zinc,—only 0·31 of the arsenic present is deposited on the platinum, and on the bladder; the rest volatilizes in the form of arseniuretted hydrogen. (Buchner, *Repert.* 21, 14.)

The liquid in contact with the negative metal is the solution of a heavy metallic salt.—The circuit composed of zinc, dilute sulphuric acid, sulphate of copper, and metallic copper, (or platinum), produces, as shown by Daniell, a very powerful current, which,—when the weakening of the solution of sulphate of copper occasioned by the deposition of metallic copper on the platinum or copper plate is made up by the addition of fresh sulphate of copper—is likewise of constant strength. [The zinc takes up oxygen from the water,—the hydrogen of which, being carried by transposition to the oxide of copper, takes up the oxygen of that compound,—whilst copper is deposited on the negative metal. Consequently, the zinc has no longer to overcome the stronger affinity of hydrogen for oxygen, but only the much weaker affinity of copper for oxygen: the solution of the zinc is thus accelerated, and the current thereby increased. If the zinc were placed in the solution of sulphate of copper as well as the platinum, it would become covered with copper, in consequence of pure chemical action taking place at the same time,—and this deposition of copper would give rise to local electro-chemical action, by which the current would be greatly weakened.]

This circuit, however, does not yield nearly so much electricity as that in which strong nitric acid is used (p. 391) [because the affinity of copper for oxygen is greater than that of nitric oxide for that element]. With the same extent of metallic surface, the circuit composed of zinc, dilute sulphuric acid, concentrated nitric acid, and platinum,—yields in a given time seventeen times as much electricity as zinc, dilute sulphuric acid, sulphate of copper, copper. (Jacobi.)—A solution of chloride of platinum in water likewise gives a current, the quantity of which is only two-thirds of that of the nitric acid circuit. (Poggendorff.)

When the circuit of zinc, sulphuric acid, sulphate of copper, and copper, is closed, the quantity of zinc dissolved in a given time is ten times as great as when it is broken. (Matteucci.)—If an amalgamated zinc plate in a circuit of this kind lose 6 grains in half a second when the surface of the copper plate is of the same size as that of the zinc,—then, when the copper surface is twice as great, the loss of weight will be 7 gr.—with 4 times the surface of copper, 9 gr.—with 8 times the surface, 13·3 gr.—with 16 times the surface, 11·5 gr.—and with 20 times the surface, 10 gr. Hence, the action is most energetic when the surface of the copper amounts to 8 times that of the zinc. (Binks.)

Zinc, solution of sal-ammoniac, solution of sulphate of copper, and copper, likewise gives a very strong and constant current. (Mullins.)—*Jacobi's Chamber Battery:* A wide, shallow, cylindrical copper vessel contains solution of sulphate of copper, which is continually kept nearly saturated by means of crystals of the salt contained in a sieve at the side. In this vessel is immersed a somewhat narrower wooden hoop tied with bladder underneath, filled with dilute solution of sal-ammoniac, and containing a round piece of zinc.

If solution of nitrate of silver be carefully poured on the top of a solution of nitrate of copper, and a copper rod dipped only into the

former, a silver tree is at first produced;—but, as soon as this tree has grown downwards as far as the copper solution, metallic copper is deposited upon it. (Grotthuss.)

If a tube tied over with bladder (*App.* 7) contains acetate of lead with platinum dipping into it, and the outer vessel *b* hydrochloric acid (or sulphate of soda,—*H. Rose*) with zinc, a lead tree is formed on the platinum. If *a* contains nitrate of silver instead of acetate of lead, the platinum becomes covered with silver. (Singer.)—When solution of common salt is used in place of hydrochloric acid, the deposition of silver on the platinum likewise takes place—according to H. Rose; but, according to Pfaff, the precipitation of silver does not take place till a little hydrochloric acid has been added to the common salt, when it commences suddenly and rapidly increases. After the precipitation of the silver, carbonate of soda collects in *a*, in the course of three weeks,—and the surface of the bladder which dips into *b* becomes covered with a thick crust of chloride of silver. If the zinc and platinum are not connected, no reduction of silver or precipitation of chloride of silver takes place, even in a fortnight. (Pfaff.)—If *a* contains nitrate of silver with graphite, *b* solution of common salt with silver free from copper, silver is deposited on the graphite in brilliant laminæ; but the action soon ceases. (Pfaff.)—[Silver has greater affinity for chlorine than for oxygen; the silver wire therefore takes chlorine from the chloride of sodium, separates silver by transposition from the nitrate of silver, and deposits it on the graphite. The action ceases as soon as the silver becomes covered with chloride.]

If the arm *a* of the U-tube (*App.* 4) contains dilute sulphuric acid with zinc, and the arm *b* nitrate of zinc with copper, zinc is deposited on the copper. (Ohm.) [I obtained no reduction of zinc.]

When zinc is placed in a saturated solution of sulphate of zinc, and copper in a saturated solution of nitrate of copper, a somewhat stronger current is produced than when both metals are immersed in dilute acid. The deflection of the needle is not increased by the addition of nitric acid to the nitrate of copper. If both vessels contain solution of sulphate of zinc or dilute sulphuric acid, the deflection is greatly increased by the addition of a little nitric acid or nitrate of copper to the liquid into which the copper dips; whereas, nitric acid added to the liquid containing the zinc diminishes the deflection. (Becquerel.)

If the tubes *a b* (*App.* 8) are stopped at the bottom with clay,—*a* containing hydrosulphate of potash (which has been exposed to the air) with antimony immersed in it, and *b* nitrate of copper with copper, and both being immersed in a conducting watery liquid,—then, when the two metals are connected, the copper becomes coated with precipitated copper; whilst on the antimony, and on the sides of the tubes, there is deposited, —first a brown-red powder, then red octohedrons and laminæ (which Becquerel considers to be kermes-mineral).—If tin be substituted for antimony—small, white, metallic-shining cubes of sulphuret of tin are deposited upon it.—With iron, when the access of air to the tube *a* is completely shut off, yellow cubes of iron pyrites are sometimes obtained. (Becquerel.)

The vessel *b* (*App.* 7) always containing solution of sal-ammoniac with zinc,—and the tube *a*, which is tied over at the bottom, containing a copper wire with a heavy metallic solution,—the following results are obtained, differing according to the nature of the liquid.—Dilute nitrate of bismuth: After two hours, a black film on the copper, increasing and becoming flocculent.—Sulphate, nitrate, or acetate of zinc: A little hydrogen is evolved

upon the copper, but no zinc is deposited.—Protochloride of tin dissolved in alcohol: After some hours—tin, in granular and needle-shaped particles, is deposited on the copper.—Dilute solution of acetate of lead: A lead tree on the copper, after a short time.—Solution of one part of green vitriol in 8 parts of water: Hydrogen gas is evolved on the copper, which in a few hours, becomes covered with a green deposit. This deposit increases considerably in a few days, and is found to consist of three layers, the outermost being hydrated protoxide of iron—the second, protoxide (black oxide?),—and the innermost, metallic iron.—Acetate of copper: The dissolved copper is deposited in the crystalline form on the copper wire.—Solution of one part of protochloride of mercury in 24 parts of water: The copper suddenly becomes covered, first with a white film of calomel, then with a grey film of mercury; on the following day, black vegetations of suboxide of mercury make their appearance.—Solution of one part of nitrate of silver in 8 parts of water: A shining silver tree immediately appears on the copper; on the bladder is deposited a considerable quantity of oxide of silver, together with black peroxide.—Solution of one part of chloride of gold in 30 parts of water: A black deposit immediately appears on the copper, soon becoming brownish and flocculent, and rapidly increasing.—Chloride of platinum: The copper becomes covered in the course of two hours with brilliant white platinum, from which laminæ subsequently separate. (Simon.)

Tube *a* (*App.* 7), containing dilute sulphuric acid with zinc, and vessel *b* a metallic salt, together with a piece of easily fusible metal,—acetate of lead yields grey crystals of lead, which grow from the piece of alloy to the height of three inches,—extending to the bladder, and covering it with a network of lead. Nitrate of silver behaves in a similar manner, the crystals of silver continuing to grow till they come in contact with the zinc. (Solly, *Phil. Mag. J.* 16, 312.)

A tube tied over with a bladder contains dilute acid, with a piece of zinc in contact with the bladder, and is immersed in a metallic solution;—the zinc is deposited on the metal, at first, by purely chemical action; but the action is afterwards propagated electrically through the bladder,—and thus the same circuit of two metals and two liquids is produced.—In the same manner, according to Wach, very solid metallic vegetations are formed; *e. g.*—with chloride of antimony: a solid mass, with individual projections;—with dilute acid solution of nitrate of bismuth: solid hemispherical masses;—with acid solution of protochloride of tin: tin-white slender ramifications;—with solution of one part of chloride of platinum in 8 parts water: solid, acute, steel-grey vegetations. If the tube contains mercury instead of zinc—and the outer vessel, nitrate of silver,—silver-amalgam is obtained in rhomboidal dodecahedrons, often elongated into six-sided prisms. (Wach.)

Likewise, when a tube, sealed at the bottom, but having a crack in it, and containing solution of sal-ammoniac with zinc, is immersed in a solution of sulphate of copper, containing a piece of metallic copper,—copper is reduced on the latter, though very slowly.

When zinc or iron is placed in immediate contact with solution of copper, that metal is precipitated in a loose pulverulent form. If the zinc or iron is surrounded with a piece of bladder, the precipitate is still loose; with two layers of bladder, it is more solid; and with three layers, very solid, knobby, and branching. [The copper first precipitated on the zinc extends itself by electric action through the layers of bladder into the copper solution; and thus an arrangement is formed, consisting of two

metals and two liquids, the solution of copper, and the moisture of the bladder.] In a similar manner, solid copper is obtained when—the tube *a* (*App.* 7) being filled with water—a piece of iron is placed in it, in contact with the bladder tied over its lower end, and the tube is immersed in a solution of sulphate of copper. In the course of two hours, copper begins to collect on the outside of the bladder; and in about a fortnight, a cake of metal is formed, with small square faces or roundish protuberances, of specific gravity 8·965, and possessed of almost perfect malleability. With zinc, instead of iron, long ramifications are obtained in the course of a month.—A zinc wire dipping into *a*, and a copper wire into *b*—the latter, when deeply immersed, becomes coated with shining, crystalline, warty, and knobby copper. Red and yellowish red octohedrons of copper are also produced,—the latter being formed when the copper solution contains no free acid, and containing an admixture of zinc. When the copper wire dips in but a little way, it becomes covered with loose ramifications. Again, if the tube *a* be closed with elder-pith, very thin cork, or very thin slate, instead of bladder,—solid copper is deposited on the outer surface of the diaphragms; much more slowly, however, when either of the two latter is used. (Wach.)

Silver, gold, and platinum may likewise be obtained in the solid state by Wach's method; silver, best by zinc,—gold, and platinum by iron. Silver separates either in ramifications or in solid plates; gold and platinum in warty concretions. (Gobel, *Schw.* 60, 414.)

If the tube tied over with bladder does not contain any liquid, but only a piece of zinc,—then, on immersing it in a solution of cadmium, grey moss-like cadmium is deposited on the bladder; in protochloride of tin, rectangular needles, an inch long, are formed; in solution of acetate of lead, a continuous plate composed of four-sided tables; in sulphate of copper, solid, malleable, warty copper; in nitrate of silver, cubical and moss-shaped silver; in chloride of gold, a non-crystalline film:—all these deposits are formed on the outside of the bladder.—In solution of arsenious acid in hydrochloric acid, arsenic is deposited, not on the bladder, but on the inner sides of the tube; in protochloride of iron, no reduction takes place.—If the tube contains mercury instead of zinc, and is immersed in a solution of nitrate of silver, elongated rhombic dodecahedrons are formed. In all these cases, the outer liquid rises by endosmose into the tube, because the zinc solution which is forming continually increases in strength. (Elsner, *J. pr. Chem.* 22, 339.)

Two Metals and three Liquids.

The two metals connected together dip into two liquids, which are united through the medium of a third. For this purpose, *App.* 2 may be used, when the wire or siphon *h* contains the third liquid,—*App.* 4, when the third liquid, being the heaviest, can be made to occupy the lower part of the U-tube,—*App.* 7, when the tube *a* is stopped at the bottom with clay, and this is saturated with the third liquid,—*App.* 8, in which the two tubes *a*, *b*, closed at the bottom with bladder or with clay, dip into the liquid in the vessel *c*. In many cases, the third liquid plays no particular part, but merely serves as a medium through which the transposition of atoms may be continued from the first to the second liquid, or *vice versâ*. We shall here notice only those cases in which one or more of the elements of the intervening liquid give rise to the formation of peculiar products in the first or second liquid.

When the tube (*App.* 7) is stopped with clay saturated with solution of nitre, and contains alcohol and a leaden wire, whilst a copper wire connected with the latter dips into a solution of blue vitriol in the vessel *b*,—copper is reduced on the copper wire, and the lead becomes covered with nitrate of lead: because the sulphuric acid of the blue vitriol liberates nitric acid from the nitre in the clay; and this nitric acid, together with oxygen, goes over to the lead. (Becquerel.)

If the cup *a* (*App.* 2) contains an alcoholic solution of sulpho-carburet of potassium, cup *b* solution of sulphate of copper—the two cups being connected by a bent tube filled with solution of nitre, and lead being immersed in *a*, and copper in *b*—reduced copper is deposited on the latter; whilst nitric acid is transferred towards the lead,—and, by its oxidating action on the sulpho-carburet of potassium, causes bicarbonate of potash and needle-shaped carbonate of lead, together with rhombic octohedrons of sulphur, to be deposited in the cup *a* and on the lead. (Becquerel.)

4. *One Metal and two Liquids. Bucholzian Circuit.*

When the same metal, either in one piece or in two pieces metallically connected, is immersed in two different liquids which touch one another, either immediately or through the medium of a porous connecting body, the part of the metal situated in one of the liquids often takes up one or more of the electro-negative elements of this liquid;—and, at the same time, one or more of the electro-positive elements of the other liquid is deposited on the part of the metal therein immersed. In this case also an electric current is produced, positive electricity going from the latter part of the metal directly to the former, or—what comes to the same thing—from the former, through the liquid, to the latter. In short, that part of the metal which combines with the electro-negative elements of the liquid, is, according to the usual mode of expression, positive towards the other.

This case is therefore different from that already described (p. 329..., 336), in which the metal dipping into two liquids suffers no chemical alteration, but merely serves to reunite the two electricities which have been separated by the combination of the two liquids.

[A metal may be inclined to take electro-negative elements from one liquid rather than from another; *e. g.* it is more inclined to oxidate in an acid or an alkaline liquid—in which the predisposing affinity of the acid or alkali for the metallic oxide comes into play—than in a neutral solution. As soon as it does this, negative electricity is set free in it,—passes into the part of the metal situated in the other liquid,—and thence to the electro-positive element of that liquid which has been set free at that very place by transposition of atoms (p. 342,*f*). The different tendencies of the several liquids that may act on the metal to produce purely chemical or electro-chemical action, must, however, be taken into account. The electric current, which results from the combination of the two liquids—and is for the most part in the opposite direction—is so small in quantity, that it need not be taken into consideration, except in a few cases.]

In these experiments, the two liquids are either carefully disposed in a vessel one above the other (which was Bucholz's arrangement), and a metallic rod introduced in such a manner as to dip into both of them;—or Apparatus 2, 3, 4, 5, 6, 7, or 8, is made use of, by dipping into the two liquids either the two ends of a simple metallic arc, or else—in order

to observe the current—two pieces of the same metal connected by the galvanometer.

Acid and water. If a pile be constructed in the following order: Paste-board saturated with water—zinc (or tin, or charcoal)—paste-board saturated with nitric acid—paste-board saturated with water—zinc, &c. &c.,—positive electricity goes from the first piece of paste-board saturated with water, through the galvanometer, to the last piece saturated with nitric acid.—In a pile composed in a similar manner of water, one metal (the best is lead, copper, or silver), and sulphuretted hydrogen water, the current takes the opposite direction. (H. Davy.)

If both divisions (*App.* 3) contain water, no current is produced on the immersion of zinc, iron, or copper; but on adding to the water in one of the divisions, a small quantity of sulphuric, hydrochloric, or nitric acid, the metal dipping into it becomes positive (*i. e.*, positive electricity goes from the metal immersed in the water, through the galvanometer, to that which is immersed in the acid). Hyponitric acid gives a contrary result. (Ritchie, *N. Ed. J. of Sc.* 2, 150.)—If cup *a* (*App.* 2) contains water, cup *b* nitric acid, the siphon *h* solution of common salt, and copper is immersed in both cups, the copper in the nitric acid is positive. (Becquerel.) [These results, obtained by Ritchie and Becquerel, are opposed to that of Davy, as far as regards the nitric acid: difference of concentration may perhaps account for the discrepancy. With respect to Davy's result, the observation in page 344, *i.* 6, must be taken into consideration.

The same acid of different degrees of concentration. When the arm *a* of the U-tube (*App.* 4) contains concentrated, and *b* dilute nitric acid, tin immersed in the dilute acid is positive towards the same metal in the strong acid. (Faraday.)—The arm *a* (*App.* 4) containing a mixture of 49 parts of oil of vitriol and 9 of water, and *b* containing water—which, by agitation of the surface of contact, has taken up a small quantity of acid and been subsequently cooled,—iron appears strongly, and copper feebly positive in the acidulated water; tin and lead, on the contrary, are positive in the stronger acid; zinc, cadmium, and silver, give no current. (Faraday.)—The same arrangement being made with highly concentrated hydrochloric acid and water,—zinc, cadmium, tin, lead, copper, and silver, are positive in the acidulated water,—iron, first negative, then permanently positive. (Faraday.)

Zinc, cadmium, tin, lead, copper, or silver, immersed in dilute acid, (*App.* 4), is strongly positive towards the same metal immersed in concentrated acid. With silver, however, the direction is variable;—the current is often suddenly reversed, and then again resumes its former direction. (Faraday.)

Let 1 be oil of vitriol; $\frac{1}{3}$, a mixture of 1 measure of oil of vitriol with 2 measures of water; $\frac{1}{21}$, a mixture of 1 measure of oil of vitriol with 20 measures of water: tin in 1 is positive towards tin in $\frac{1}{3}$ or $\frac{1}{21}$; and tin in $\frac{1}{3}$ is positive towards tin in $\frac{1}{21}$.—Lead or copper in $\frac{1}{3}$ is positive towards lead in 1 or $\frac{1}{21}$.—Iron in 1 is negative towards iron in $\frac{1}{3}$ or $\frac{1}{21}$, and iron in $\frac{1}{3}$ is negative towards iron in $\frac{1}{21}$. (Faraday.)

Let 1 be concentrated nitric acid; $\frac{1}{2}$, a mixture of 1 measure of the same with 1 measure of water; $\frac{1}{4}$, with 3 measures of water; $\frac{1}{21}$, with 20 measures of water: lead in $\frac{1}{4}$ is positive towards lead in 1 or $\frac{1}{2}$, and lead in $\frac{1}{2}$ is positive towards lead in 1.—Copper in $\frac{1}{4}$ is positive towards copper in 1 or $\frac{1}{21}$; copper in $\frac{1}{2}$ is positive towards copper in 1, and negative towards copper in $\frac{1}{21}$. (Faraday.)

Different acids. One arm of the bent tube (*App.* 5) containing oil of

vitriol,—the other, concentrated nitric acid,—the zinc in the former is positive, but becomes negative after the circuit has been closed for some time. [In consequence of being coated with sulphate of zinc?]—Iron, copper, and silver are likewise positive in oil of vitriol, negative in nitric acid,—iron the most strongly, silver the least. Nevertheless, zinc, copper, and silver are most strongly attacked in nitric acid. Although, therefore, the greatest quantity of electricity must be set free in that part of the circuit, it becomes directly neutralized at the surface of the metal,—because the passage of positive electricity from the oil of vitriol to the other piece of metal is attended with difficulty. (De la Rive.) [Nitric acid has a peculiar inclination for pure chemical action (p. 344, *i.* 6).)]

Alkali and water. If a pile be constructed in the following order: Paste-board saturated with water—charcoal—paste-board saturated with solution of soda, &c. &c., positive electricity goes from the last piece of paste-board saturated with soda, through the galvanometer, to the first piece saturated with water. Similarly, if we arrange one above the other: Paste-board saturated with water—zinc—pasteboard saturated with water and sprinkled on the side touching the preceding zinc with hydrate of potash—zinc, &c. &c. (H. Davy.)

Alkali of different degrees of concentration. Zinc, cadmium, tin, and lead, are strongly—copper moderately—and iron slightly positive in concentrated alkali, towards the same metals in dilute alkali. (H. Davy; Faraday.)

Potash and hydrosulphuret of potassium. Zinc in potash is positive towards zinc in hydrosulphuret of potassium. Silver and palladium are negative, copper almost neutral. (H. Davy.)

Acid and alkali. Zinc, tin, lead, or copper, in strong solution of potash (*App.* 3), is positive towards the same metal in dilute sulphuric acid. In this action, the lead, tin, or amalgamated zinc, in the sulphuric acid, even becomes covered with bubbles of hydrogen gas—proceeding, not from the purely chemical action of the acid, but from the electro-chemical action of the potash,—their evolution ceasing when the circuit is closed. (Faraday.) With potash on the one side, and sulphuric, nitric, or hydrochloric acid on the other, zinc is more strongly, iron and copper less strongly positive, in potash. With dilute sulphuric acid, the current is stronger than with the same acid concentrated. (Grove.)

Water and solution of common salt. Copper in solution of common salt is positive towards copper in water. (H. Davy.)

Acids and chloride of calcium. Zinc and copper in solution of chloride of calcium (*App.* 5) are positive towards the same metals in dilute nitric acid. (De la Rive.)

Heavy metallic salts and water. If pure water be carefully poured upon a solution of chloride of zinc, and a zinc rod immersed in both liquids, zinc is deposited on its lower end. If water be placed upon a concentrated solution of protochloride of tin containing a little free acid, and a rod of tin be introduced, a portion of tin is dissolved from it in the lower liquid,—while crystalline tin is deposited upon it at the surface of contact of the tin solution and the water. (Bucholz.) But if the tin-solution does not contain free acid, a portion of tin dissolves at the surface of contact of the solution and the water, while tin is reduced on the lower part of the rod. (Ritser, *A. Gehl.* 1, 427.) A leaden rod similarly immersed in water and solution of nitrate of lead, becomes corroded above and covered with reduced lead below. A similar effect is produced, when a saturated solution of nitrate of copper is placed at the bottom of a tube, water above it, and a copper rod immersed in both,—the action being particu-

larly strong when a small quantity of nitric acid is added to the water. (If the water by chance remains unmixed, no action is apparent; but if it contains a little nitrate of copper, the action commences immediately. *Gm.*) In all these cases, and those yet to be described—as recorded by Bucholz—the metallic rod is found to remain unaltered for a small space between the part at which it becomes corroded and that at which reduced metal is deposited upon it. (Bucholz, *A. Gehl.* 3, 324 and 424; *N. Gehl.* 5, 127.) A rod of silver, dipping into water and solution of nitrate of silver, becomes corroded and acquires a brown colour in the water—whilst silver is precipitated on the lower part, which is immersed in the silver solution. (*Grotthus.*) If two pieces of zinc, iron, or manganese are immersed in water and the aqueous solution of the corresponding sulphate, the piece immersed in this solution becomes positive and oxidizes. (Becquerel.)

Heavy metallic salts and acids. Dilute nitric acid being placed on a solution of nitrate of lead, or dilute acetic acid upon acetate of lead, an immersed leaden rod becomes corroded above and coated with metallic lead below. A similar effect is produced upon a copper rod immersed in dilute nitric acid and nitrate of copper, or dilute sulphuric acid and sulphate of copper. So likewise with a silver rod in water containing a little nitric acid and a neutral solution of nitrate of silver. In all these cases, the metal corrodes in the acid, and becomes coated with reduced metal in the metallic solution. (Bucholz.) In a concentrated solution of sulphate of copper covered with dilute nitric acid, a copper rod becomes coated with small metallic octohedrons. (Elsner.)

Heavy metallic salts and ammonia. The lower stratum consisting of sulphate of copper dissolved in water acidulated with sulphuric acid, the upper of ammonia,—a copper wire immersed for twelve hours in these liquids becomes corroded in the copper solution, and covered with crystals of copper in the ammonia. (Berzelius, *Lehrbuch.*)

Heavy metallic salts and sulphuret of carbon. If aqueous solution of nitrate of copper be placed above sulphuret of carbon in a glass tube sealed at the bottom, and a plate of copper immersed in these liquids, crystals of suboxide of copper form on its upper part; and carbon (sulphuret of copper? *Gm.*) is deposited on the tube in thin laminæ, possessing the metallic lustre.

Heavy metallic salts and alkaline salts. Cup *a* (*App.* 2) containing common salt, and cup *b* sulphate of zinc,—zinc immersed in the latter is positive: so likewise, iron dipping into common salt and protosulphate of iron.—But copper in nitrate of copper is negative towards copper in common salt;—similarly, with lead in nitrate of lead and common salt [with nitric acid and heavy metallic nitrates there is a peculiar tendency to pure chemical action].—The U-tube (*App.* 4) containing asbestus at *h*, solution of chloride of barium at *a*, and solution of chloride of lead at *b*, and the ends of an arc of lead dipping into the two arms of the tube,—shining, silky crystals are formed on the lead in *a* [which is therefore positive];—these crystals appear to be a combination of chloride of lead with chloride of barium.—If the arm *a* contains solution of common salt with crystals of the same—the arm *b*, solution of sulphate of copper with oxide of copper,—and the ends of a copper wire dip into the two arms,—copper is deposited on the end immersed in the blue vitriol, which is negative. The sulphuric acid thereby liberated dissolves the oxide of copper,—and the copper in the salt solution, which becomes alkaline [because the sulphuric acid does not pass over, and the oxygen of the oxide of copper combines with the sodium of

the common salt and sends chlorine to the copper], covers itself with octohedrons—which appear to be a combination of subchloride of copper with chloride of sodium, and give up the latter to the water:—they are at first transparent and colourless; but when the experiment lasts two or three months, they become first violet and afterwards emerald green, remaining however transparent. [Protochloride of copper + chloride of sodium?]—When sal-ammoniac is used in this experiment instead of common salt, and the air is kept from the arm *a*, octohedrons with truncated edges and summits,—at first colourless, but afterwards acquiring an amethyst tint—are deposited on the copper in the sal-ammoniac, and sometimes six-sided prisms upon these. Both these compounds are decomposed by water, which extracts the sal-ammoniac. Nitrate of copper behaves with common salt and sal-ammoniac just like sulphate of copper. Chloride of potassium or chloride of barium substituted for common salt, deposits on the copper similar compounds of chloride of copper with chloride of potassium or chloride of barium in tetrahedrons. Silver immersed in nitrate of silver and aqueous solution of sal-ammoniac, chloride of potassium, chloride of sodium, or chloride of barium, covers itself in like manner, in the last mentioned solutions, with octohedral or tetrahedral combinations of chloride of silver with these metallic chlorides. Tin dipping in the same manner into common salt and sulphate of copper, covers itself in the former with needles of chloride of tin and sodium—and lead, with tetrahedrons of chloride of lead and sodium. (Becquerel.)

If solution of sal-ammoniac or common salt be poured upon pulverized oxide of lead in a tube sealed at the bottom, and a rod of lead immersed so as to touch the oxide, reduced lead is deposited upon it. When solution of sal-ammoniac is placed above peroxide of lead, an immersed leaden rod becomes covered with needles, from which water extracts sal-ammoniac,—probably therefore chloride of lead and ammonium. [In the first place, oxide of lead dissolves at the lower part in sal-ammoniac or common salt: two liquids are thus formed: the former yields chlorine to the lead; the latter deposits reduced lead, if protoxide of lead has been used—or when peroxide of lead is employed, extracts oxygen from it.]—In like manner, a copper rod dipping into oxide of copper and solution of sal-ammoniac—access of air being prevented—becomes covered with large crystals, consisting of a combination of subchloride of copper with sal-ammoniac—colourless at first, afterwards acquiring a yellow tint, and differing in form from those previously mentioned (p. 400). (Becquerel.)

If the tube stopped at the bottom with clay (*App.* 8), contains solution of iodide of potassium—the tube *b* solution of nitrate of lead—the vessel *c* any conducting watery liquid—and the ends of an arc of lead dipping into *a* and *b*,—white silky needles of iodide of lead and potassium are deposited upon the lead in *a*, gradually decomposing, and changing into octohedrons of iodide of lead.—If *a* contains iodide of potassium or sodium, and *b* sulphate of copper, metallic copper is deposited on the lead in *b*; and on the lead in *a*, long silky needles of iodide of lead and potassium, or iodide of lead and sodium, from which water extracts iodide of potassium or sodium.—Copper treated in the same manner gives, at first, white needles of iodide of copper and potassium, then—after their decomposition—octohedrons of iodide of copper. (Becquerel.)

Tube *a* (*App.* 8), containing hydrosulphuret of potassium, which should be slightly decomposed by exposure to the air, and tube *b* containing nitrate of copper, sulphuret of copper and potassium is at first deposited on the copper in *a* in fine silky needles; these, however, are gradually

decomposed, and converted into grey, metallic-shining crystals of disulphuret of copper with triangular faces.—If the copper salt be replaced by nitrate of silver, and the copper arc by a silver arc, the silver in *b* becomes covered with silver, and the silver in *a* with beautiful prisms of sulphuret of silver and potassium, which are gradually decomposed by the nitric acid carried over to them, so that sulphate of potash and octohedral sulphuret of silver are produced. (Becquerel.)

The tube *a* stopped with clay (*App.* 7), being filled with a solution of bicarbonate of soda, the vessel *b* with a solution of sulphate of copper, and a copper arc dipping into the liquids, copper is reduced on the copper in *b*, and bluish green silky needles of carbonate of copper and soda are deposited upon *a*. If now the carbonate of soda in *a* be replaced by water, the galvanic action becomes weaker; but the sulphuric acid which goes over from the sulphate of copper decomposes the above-mentioned double salt into sulphate of soda, and partly crystalline, partly pulverulent carbonate of copper. (Becquerel.)

Two different heavy metallic salts. Cup *a* (*App.* 2), containing sulphate of zinc, and cup *b* nitrate of copper, copper in *a* is positive towards copper in *b*: so likewise with zinc and lead. (Becquerel.)—A copper rod dipping into a vessel filled with solution of corrosive sublimate, at the bottom of which is placed a piece of copper [a portion of which dissolves, and so forms the second liquid], becomes covered with metallic-shining lamina of chloride of mercury and copper. (Becquerel.)

One metallic salt with different proportions of acid. The cups *a*, *b* (*App.* 2), containing the same solution of chloride of antimony, and a bar of antimony connected with the galvanometer dipping into both of them—a current is produced, as soon as a portion of acid is introduced into the cup *a*, the antimony immersed in the acid solution becoming positive. So likewise with chloride of bismuth and metallic bismuth; with sulphate of tin and metallic tin; with chloride of lead and metallic lead; with chloride of iron and metallic iron; with nitrate of copper and metallic copper.—But with sulphate of zinc or protosulphate of iron, on the contrary, the zinc or iron in the acidulated solution becomes negative. (Becquerel.)

When acetate of lead is poured upon pulverized litharge in a glass tube, and a bar of lead immersed in both, protoxide of lead in dodecahedrons and needles is deposited upon it.—If the tube contains pulverized oxide of copper, a saturated solution of nitrate of copper, and a copper rod—the tube being also well closed—metallic-shining octohedrons or cubes of suboxide of copper are deposited on the rod in ten or fourteen days. If the tube contains much oxide of copper, the liquid in the course of half a year completely loses its colour, and is then found to contain nitrate of ammonia. When the quantity of oxide of copper is smaller, the liquid remains coloured—and the crystals of suboxide of copper formed at the beginning lose their lustre, and take up nitric acid.—When oxide of copper and aqueous solution of chloride of copper are placed in the closed tube, the liquid loses its colour; and on the copper rod is deposited crystallized subchloride of copper—which, on the side turned towards the light, becomes covered with capillary crystals of suboxide. (Becquerel.) [How much in these experiments is to be attributed to electro-chemical, and how much to purely chemical action, is yet to be determined.]

5. The four ends of two metallic arcs dip into two separate vessels filled with liquid.

In these cases, one of the liquids is decomposed by the metal, the other by the electric current thus produced.

A. *The same liquid in both vessels.*

a. Two Metals.—The ends of both metals dip into one vessel, the ends of one metal only into the other vessel.

In the following experiments, Faraday made use of *App.* 19. The platinum wire *o* which dips into the glass vessel *a*, is continued by the galvanometer, and connected by the iron wire *y z* with the platinum wire *p*, which dips into the vessel *b*. The iron, nickel, or silver wire dipping into *a* is connected at *x* with the platinum wire *i* which dips into *b*.—The current excited by the iron, nickel, or silver, in connection with the platinum in the liquid of the vessel *a*, has to make its way through the liquid in the vessel *b*, which weakens and, in some cases, completely stops it.

If *a*, *b*, contain nitric acid freed by boiling from nitrous acid, the iron appears slightly positive (*i. e.*, positive electricity goes from *o* through *y*, *z*, *p*, *i*, to *g*); but the current is so feeble, that it is far exceeded by the opposite current excited by the introduction of a piece of paper moistened with hydrochloric acid, between the iron and platinum at *x*. A similar result is obtained when the end of the iron wire which dips into *a* has been made passive by ignition in the air. If the acid is diluted with four measures of water, the current is still weaker; and in both cases it is surpassed by a thermo-electric current produced by a single pair of bismuth and antimony.

When *a*, *b*, contain fuming nitric acid—which conducts better than the ordinary acid—iron produces a stronger current, which is only reduced one half by the opposite thermo-electric current of a single pair of bismuth and antimony.

If both vessels contain a mixture of equal parts of hyponitric acid and water, both ignited and unignited iron are at first slightly positive; but the current soon ceases. Unignited iron in *a* becomes passive; but the circuit still conducts a thermo-electric current well (though not nearly so well as sulphuret of potassium)—and moistened paper between the platinum and iron at *x* excites an opposite current. When the end of the iron dipping into *a* has been ignited, the circuit, after it has become inactive conducts the thermo-electric current with great facility. [Iron rendered passive by hyponitric acid is covered with peroxide of iron, which is not quite so good a conductor as the black oxide ($Fe^3 O^4$), with which iron rendered passive by ignition is coated.]

In concentrated aqueous solution of potash, silver gives scarcely any current; iron or nickel, a feeble current which soon diminishes. When the solution of potash is diluted with six measures of water, silver gives no current, nickel or iron a feeble one, which, however, continues for a longer time. In these cases, paper wetted with nitric acid, introduced at *x*, excites an opposite current of greater strength.

If the cups *a*, *b*, contain yellow solution of sulphuret of potassium, the iron appears negative towards the platinum for ten minutes, on account

of the oxide which adheres to it. After this, the current ceases altogether. Nevertheless, the circuit conducts admirably—and produces a thermo-electric current on the application of heat at x, y, or z (where the iron and platinum touch one another)—and a galvanic current of still greater power on the introduction of paper moistened with dilute acid between the two metals.—It appears then that no current is excited by the contact of two heterogeneous metals at x (the effects of contact at y and z would neutralize each other); but when the metals are separated at x by a moist conductor, a current is produced.—Just as platinum behaves with iron in solution of sulphuret of potassium, so also does gold behave with iron or nickel, and palladium with iron or nickel: the slight deflection of the needle which always takes place at first, soon ceases. Only in the case of platinum with palladium, is the very feeble current of longer duration—the palladium after some time becoming covered with sulphuret of palladium. (Faraday.)

If the cups a, b (*App.* 2) contain solution of nitrate of silver—the arc $g\,i$ consisting of silver, the arc $o\,p$ of zinc at o and of silver at p—a silver tree is formed at p and g, and likewise [by purely chemical action] on the zinc, whilst the silver end i dissolves. (H. Rose.)

The cups a, b (*App.* 2), containing solution of nitre—o being zinc, p platinum, and $g\,i$ zinc—the current is stronger than when a and b are connected by a bundle of threads saturated with solution of nitre, instead of by the arc of zinc. (H. Davy.) In Faraday's experiments, three ends of the less oxidable metal are used; in those of Davy, three ends of the more oxidable metal. (*Vid. Decompositions by the electric current, Diaphragms.*)

b. Three Metals and one Liquid. One metallic arc consists of two different metals, the other of the third metal.

The cups a, b (*App.* 2), containing a solution of copper, and o consisting of zinc, p of silver,—copper is precipitated on the silver, provided the second metallic arc $g\,i$ is formed of one of the more oxidable metals, not of gold or platinum. (Singer.)

The vessels a and b (*App.* 2), containing solution of nitrate of silver, and o consisting of zinc, p of platinum, $g\,i$ of silver,—silver is reduced at o, p, and g, while the silver end i dissolves. [The zinc as it oxidates sends negative electricity to the platinum—which negative electricity combines with the silver there reduced; the silver reduced by zinc in a is deposited, partly on the zinc by purely chemical action, partly on the silver end g by electro-chemical action. The negative electricity which has to combine with the silver reduced at the end g receives it from the silver end i, from which negative electricity is set free by the combination of the silver with oxygen.]—When the silver arc $g\,i$ is replaced by an arc of platinum, the action is much slower [because the platinum end i takes up no oxygen, and therefore gives rise to no transposition of atoms in b].—If the vessels a, b, contain solution of sulphate of copper, and $g\,i$ consists of silver, copper is deposited on the zinc [by purely chemical action], and likewise, after twenty-four hours, on the platinum and on the silver end g [silver probably also dissolving at i].—When the arc $g\,i$ consists of platinum, the platinum b does not become covered with copper till after the lapse of two days; but the action is much more energetic when the arc $g\,i$ [illegible]med of zinc, tin, lead, or iron. (Pfaff.)

[illegible] the vessels a, b (*App.* 2) contain a mixture of 1 part of oil of [illegible] and 100 parts of water, $o\,p$ being an iron wire coated at p with

peroxide of lead, and *g i* a platinum wire,—hydrogen gas is evolved at the platinum end *g*, and oxygen at the platinum end *i*. (Schönbein.)

The metallic arc *o p* (*App.* 2), consisting of platinum dipping into *a* by a point, but into *b* by a large surface, and the cups *a*, *b* containing water, or a mixture of 1 part oil of vitriol and 10 parts water, or 1 part oil of vitriol, 5 parts common salt, and 100 parts water, or a mixture of sea-water and nitric acid,—a larger deflection is produced when the arc *g i* consists of zinc at *i* and copper at *g*, than when it is arranged the contrary way. But with a mixture containing from 1 to 18 parts oil of vitriol with 1000 parts water, or 1 part hydrochloric acid and 80 parts water, the strongest deflection is produced with zinc in *a* and copper in *b*. With 1 part of common salt in 10 of water, the deflection is equally strong both ways. (Marianini.)

Various combinations with three and four metals.

The vessels *a*, *b* (*App.* 2), containing either pure or acidulated water, the current produces the same deflection of the needle in each of the following three combinations: 1. *o* zinc, *g* platinum, *p* and *i* copper;—2. *o* zinc, *p* platinum, *g* and *i* copper;—3. *o* zinc, *p* copper, *g* platinum, *i* iron. (Poggendorff.)

If both vessels contain water acidulated with sulphuric acid, *o* being cadmium, *g* iron, *p* platinum, and *i* copper, the current excited by copper with platinum has the advantage over that produced by cadmium with iron; whereas a simple circuit of cadmium and iron produces an electric current 400 times as strong as that excited by a copper and platinum circuit.

B. *Two Liquids and two Metals.*

a. Each metallic arc consists of one metal.

This arrangement may be regarded as a combination of two circuits of two metals and one liquid—or, according to Pohl, as a combination of two circuits of one metal and two liquids.

Experiments of this kind may be made with *App.* 2;—*App.* 20. (The upper end of one of the metals is bent round, and either beaten out flat or hollowed into a cup; and in or upon this is placed a liquid or a piece of paper saturated with a liquid, with which the bent wire *i* of the other metallic plate *g* is connected);—*App.* 21. (The two bent tubes are filled with the two liquids, in which are immersed the four ends of the two metallic arcs.

If the cup *a* (*App.* 2), contains oil of vitriol, and *b* nitric acid—the arc *o p* consisting of platinum, *g i* of zinc, tin, lead, iron, copper, brass, or silver—positive electricity goes from the oil of vitriol, through the galvanometer interposed in the platinum arc, to the nitric acid. Hence the galvanic action of the oil of vitriol on the more oxidable metal overcomes that of the nitric acid. The contrary effect is generally produced, if the cup *a* contains solution of chloride of calcium instead of oil of vitriol; but the current is feeble. (De la Rive.)

The cup *a* (*App.* 20) containing water mixed with sulphuric acid and a little nitric, the arc *o p* being formed of zinc and *g i* of platinum, and a piece of paper saturated with iodide of potassium being placed between *p* and *i*,—iodine is separated upon the platinum; and when turmeric paper is used, it is turned brown from the liberation of alkali on the zinc *p*.

The same decompositions of the second liquid are obtained with zinc, platinum, and aqueous solution of potash or common salt; and likewise (as Andrews obtained them with *App.* 19), with amalgamatedz inc, platinum, and water merely acidulated with sulphuric acid. In these cases, the action of the liquid containing acid or common salt upon the zinc overcomes that of the solution of iodide of potassium on the same metal. In this or a similar manner, zinc with platinum in dilute sulphuric acid decomposes aqueous solution of iodide of potassium, fused protochloride of tin, and fused chloride of silver—but not water acidulated with sulphuric acid, hydrochloric acid, solution of Glauber's salt, fused chloride of lead, or fused iodide of lead. In those cases in which no decomposition takes place, there is likewise no current produced.—Zinc and platinum in aqueous solution of potash, or a mixture of ammonia and sulphate of ammonia, decomposes aqueous solution of iodide of potassium, sulphate of soda, nitrate of silver, and hydrochloric acid.—Zinc and platinum in water containing both sulphuric and nitric acid, decomposes not only the above named compounds, but also fused nitre, fused chloride of lead, and fused iodide of lead, but not solution of acetate of lead. It is not the quantity but the intensity of the current that determines the decomposition of these compounds: large plates of zinc and platinum in water containing sulphuric acid do not decompose the last mentioned substances; but the decomposition takes place readily, even with wires of these metals, if the water contains nitric in addition to the sulphuric acid. At all events it follows from these experiments, that contact of metals is not essential to the production of an electric current.—Polished lead with platinum in water likewise produces a current capable of decomposing iodide of potassium. (Faraday.)

Water containing sulphuric acid being placed in the vessel *a* (*App.* 2), aqueous solution of potash in *b*, and the ends of the zinc arc *o p* and of the copper or platinum arc *g i* dipping into both liquids,—a current is at the first instant produced in favour of the potash (from *o* to *p*)—but it ceases immediately. (Faraday.)

The arc *o p* (*App.* 21) consisting of platinum, the arc *g i* of some other metal, and the tubes *a*, *b*, containing different liquids—an electric current, generally a strong one, is produced in the direction *a o p b*, when the liquids and metal are disposed in the following order: *g i* iron, *a* dilute sulphuric acid, *b* fuming nitric acid;—*g i* iron, *a* hydrochloric acid, *b* hyponitric acid diluted with water sufficient to make it green;—*g i* zinc, cadmium, lead, or copper, *a* hydrochloric acid, *b* iodide of potassium;—*g i* iron, *a* dilute hydrochloric acid, *b* fuming nitric acid or yellow solution of sulphuret of potassium;—*g i* iron, *a* dilute nitric acid, *b* concentrated colourless nitric acid, fuming nitric acid, hydrated green hyponitric acid, or yellow solution of sulphuret of potassium;—*g i* iron, zinc, cadmium, lead, or copper, *a* dilute nitric acid, *b* iodide of potassium;—*g i* iron, *a* water or solution of common salt, *b* hydrated green hyponitric acid.—If the arc *o p* consists of iron instead of platinum, the current takes the same direction with the following arrangements: *g i* zinc or lead, *a* oil of vitriol, *b* dilute sulphuric acid;—*g i* copper, *a* yellow sulphuret of potassium or strong nitric acid, *b* dilute nitric acid or iodide of potassium. The galvanic action of the liquid contained in *a* always predominates. (Faraday.)

Poggendorff, by the use of *App.* 2, obtained currents, feeble for the most part, and varying, not only according to the liquids used, but likewise according to the nature of the meta[illegible] acids used were very dilute;

+ denotes that the galvanic action is strongest in the vessel *a*, — the contrary; ± denotes that the current takes the former direction at first and afterwards the latter; ∓ the contrary.

In Vessel.		Zinc with				Amalgamated zinc with					Tin with			Iron with			
a.	*b*.	Pt.	Ag.	Cu	Sn.	Pt.	Ag.	Cu	Sn.	Fe.	Zn.	Pt.	Ag.	Cu	Pt.	Ag.	Cu	Sn.
Sulphuric acid	Water	+	−	−	−	±	−	−	−	±	+	−	−	+	±	0	−	−
„	Sal-ammoniac	−	−	+	−	−	.	.	.	−	.	.	.	.	−	.	−	.
„	Iodide of potassium.	−	+	+	−	−	+	+	−	−	+	+	+	+	−	−	−	+
„	Borax	+	+	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.
Hydrochloric acid	Water	−	−	−	−	.	.	.	.	.	.	.	.	.	.	.	.	.
„	Sal-ammoniac	∓	−	−	−	.	.	.	.	.	.	.	.	.	.	.	.	.
„	Common salt.....	+	−	−	−	.	.	.	.	.	.	.	.	.	.	.	.	.
„	Iodide of potassium	−	+	+	−	−	+	+	∓	∓	∓	+	+	+	+	+	+	−
Nitric acid.....	Water	+	−	−	0	.	.	.	+	.	+	−	−	−	.	.	−	.
Ammonia.....	Water	+	+	−	+	+	+	−	−	+	+	−	−	−	−	−	−	−
Potash	Water	+	+	+	−	+	+	+	−	+	+	0	+	+	−	−	−	−
Carbonate of soda.....	Water	−	−	−	−													
Common salt.....	Water	±	−	−	0													
„	Sal-ammoniac	−	−	−	−													
Borax	Sulphate of magnesia	−	−	−	−													
„	Sulphate of zinc ...	−	−	−														

The direction of the current varies with the degree of concentration. With zinc and platinum, hydrochloric acid produces a stronger current than iodide of potassium; but with dilute acid the contrary effect is observed. With zinc and copper, dilute hydrochloric acid also has the preponderance, [because the copper takes up iodine]. Sulphuric acid with platinum and zinc is overcome by iodide of potassium [Faraday asserts the contrary]; and with a mixture of one measure of oil of vitriol and two measures of water, no current is produced. (Poggendorff.)

The arc *o p* consisting of platinum, the arc *g i* of zinc, and the two vessels *a*, *b*, containing water—then, if from any inequality in the zinc plates, a feeble current is produced proceeding from *a* to *b*, this current is actually strengthened by the introduction of common salt into *b*—although this substance, by increasing the chemical action in *b*, might be expected to produce an opposite current. Nitric acid introduced into *b* likewise strengthens the current in many cases, but sometimes changes its direction. (Poggendorff.)

When the vessels *a*, *b* (*App.* 2), contain water, and *o p* consists of platinum, *g i* of zinc, no current is apparent, even on heating one of the vessels to the boiling point, although the chemical action must be thereby increased: but the addition of a small quantity of acid or salt to the water in one of the glasses immediately excites a current. (Poggendorff.)

If the cup *a* (*App.* 2) be divided into two parts by a membranous diaphragm—the left hand division in which the platinum arc *o p* is immersed containing nitric acid, while the right hand division into which the arc *g i* is made to dip, and likewise the cup *b*, are filled with a mixture of one measure of oil of vitriol and three measures of water—a feeble current is excited in favour of the cup *a*; but the zinc in *b* is most quickly dissolved. (Poggendorff.)

b. One metallic arc is formed entirely of one metal, the other arc half of one metal, and half of the other.

The arc *o p* (*App.* 2) consisting of platinum, the arc *g i* half of copper, half of platinum,—also one of the cups containing oil of vitriol, the other, nitric acid,—the deflection amounts to only 5°, when the copper is placed in the nitric acid; but to 40° when it is immersed in the oil of vitriol—although the solution is much more rapid in the first case than in the second:—and copper with platinum immersed in nitric acid alone, produces a deflection of 90°; and in oil of vitriol alone, a deflection of 40°. In consequence of the small conductibility [decomposibility] of the oil of vitriol, the electricity developed by the copper and the nitric acid becomes neutralized directly on the metal. (De la Rive.)

The arc *o p* (*App.* 2) and *g* consisting of copper, *i* of zinc,—or, on the contrary, *o p* and *g* of zinc, and *i* of copper,—and the cup *a* containing spring water, *b* acidulated water, or the contrary,—the current is of the same strength in all four cases: it diminishes however more quickly when the zinc is immersed in the acidulated water, than when it is placed in the spring water. (Poggendorff.)

c. Two Liquids and three Metals.

The vessel *a* (*App.* 2) containing nitric acid, *b* water, and the arc *o p* consisting of platinum, *g* of silver, *i* of copper, iron, lead, or zinc,—these last metals are positive, although they are much less attacked than the silver in the nitric acid. (Marianini.)

Addendum.

Pohl's Battery. One zinc and seven copper plates are separated from one another by seven layers of a moist conductor which does not surround them, but merely touches their surfaces. (*App.* 22; Z = zinc, C = copper, *m* = moist conductor.) The zinc at one end is connected by a metallic arc with the copper, No. 7, at the opposite end; similarly, C^1 with C^6, C^2 with C^5, and C^3 with C^4. An electric current sensible to an interposed galvanometer goes through all the arcs, through the first and third in one direction, through the second and fourth in the opposite direction. The current in the first arc is the strongest, that of the second weaker, and that of the fourth weakest of all. (Pohl.) [The zinc in connection with C^1, C^5, and C^7 furnishes an example of the case of two metals with one liquid in two vessels, described on page 403. This produces a current which goes from C^7 through the first arc to the zinc, and from C^1 through the second arc to C^5. So far the result is easily explained; but the origin of the current in the third and fourth arcs is not yet ascertained.] *Compare* Henrici. (*Pogg.* 53, 284.)

Pohl's Contracted Pile. (*Pogg.* 50, 497.)

Instruments for the production of Electric Currents by means of Chemical Action.

I. *Instruments consisting of a Simple Galvanic Circuit.*

Wollaston's Thimble Apparatus (*Gilb.* 54, 1),—the smallest simple galvanic circuit capable of igniting a metallic wire, is thus constructed. A copper thimble converted by removal of the bottom into a cylinder

opened at both ends, is beaten flat—so that the opposite sides are brought within two lines of one another. In this space, a zinc plate not quite $\frac{3}{4}$ of an inch wide is fastened with sealing wax in such a manner as no where to come in contact with the thimble. To the upper end of the thimble is soldered a loop of silver wire. A platinum wire 1 inch long and $\frac{1}{40}$ of an inch thick is soldered to the upper part of this loop, and thence, carried in a slanting direction towards the zinc. Another similar wire fastened to the zinc plate proceeds in a direction opposite to the former, the two wires being fastened into glass bulbs, and running parallel to one another for a certain distance with a very small interval between them. Lastly these two wires are connected together in the middle by a very fine wire of platinum. To obtain this fine wire, a platinum wire $\frac{1}{100}$ of an inch thick is surrounded in a mould with a bar of silver $\frac{1}{8}$ of an inch thick. The compound wire thus formed is drawn out to the thickness of $\frac{1}{100}$ of an inch; a piece of it, an inch in length, is bent round, and the bent part immersed in nitric acid—which, by dissolving the silver, exposes a platinum wire of such extreme fineness that it can scarcely be seen by the naked eye. If now the ends of this wire still retaining the silver be drawn tightly over the two thick platinum wires, soldered to them with zinc and sal-ammoniac, and then the projecting parts cut off, the two thick platinum wires will be connected by means of a wire of extreme tenuity. On immersing this apparatus nearly up to its upper rim in a mixture of one measure of oil of vitriol and 50 of water, the fine wire—whose length must not exceed from $\frac{1}{10}$ to $\frac{1}{20}$ of an inch—becomes incandescent and remains so for some seconds. [The negative electricity set free from the zinc as it dissolves combines in the very thin wire—through which it passes with difficulty—with positive electricity evolved from the thimble.]

Hare's Deflagrator and *Calorimotor*. Large continuous surfaces of zinc on the one hand and copper on the other, placed near to one another but not in contact, are immersed in an acid liquid. If the copper and zinc be then connected by a thick metallic wire, positive electricity goes from the copper to the zinc, and negative electricity from the zinc to the copper, in very large quantity—so that connecting wires, even of some thickness are heated and fused, and a piece of charcoal placed between the ends is brought into a state of vivid incandescence. But the tension of the current is as low as when a small pair of plates is used. Hence when the connection between the copper and zinc is formed by means of imperfect conductors, such as liquids, the current is nearly stopped.

Of the *Deflagrator* there are two forms: 1. A zinc plate, 6 inches broad and 9 inches long, and a copper plate, 6 inches broad and 14 inches long, are rolled up together into a cylinder $2\frac{1}{2}$ inches in diameter, in such a manner that they never come into actual contact, but remain at the distance of a quarter of an inch from one another,—the last coil of the zinc being completely surrounded by the copper. All the copper plates of eighty such rolls are united by soldering with a single metallic rod, and thus connected with each other; a similar connection is made between all the zinc plates. When these rolls, suspended by a lever, are simultaneously immersed in eighty cylindrical glasses filled with dilute acid, and the two metallic rods connected by a platinum wire $\frac{1}{4}$ inch thick, the wire is instantly melted. Copper and mercury are burnt. A leaden tube being soldered to the extremity of the wire proceeding from the copper, and a pointed piece of charcoal fixed into the tube—then, on bringing this piece of charcoal near another piece similarly fitted to the zinc side, or

near a platinum wire $\frac{1}{8}$ inch thick, connected with the zinc, a most dazzling light is produced (p. 317).

2. Two hundred and fifty zinc plates, each 3 inches wide and 7 inches long, are placed in 250 flat copper cases, open at top and bottom. Every 50 of these pairs are hung on a separate bar of wood. Each copper case is separated from the next by a covering of paste-board, coated with shellac varnish. In this manner, 50 copper cases are united into one dense mass. Under each of the 5 immovable bars is placed a trough, filled with dilute acid. All 5 troughs are placed on a common support, which can be let up and down—so that, on raising the troughs, the liquid contained in them fills the space between the zinc and copper. The effects produced by this apparatus are similar to those of the arrangement last described, or even stronger.

In the *Calorimotor*, 20 copper and 20 zinc plates, each having a surface of 19 square inches, are fastened alternately and perpendicularly in a frame: all the copper plates are soldered to one common bar, and all the zinc plates to another. The whole is immersed in a trough filled with acid, and the copper connected with the zinc by a conductor. This apparatus produces similar but less powerful effects. With from 60 to 120 copper and as many zinc plates, platinum wire may be fused, &c.

II. *Instruments formed by the union of several Simple Galvanic Circuits. Voltaic Piles in the more extended Sense,—Galvanic Batteries.*

1. *The Simple Circuits consisting of two Metals and one or two Liquids.*

When two metals *m*, *t*, are connected with a fluid with which they form a simple galvanic circuit, in the following order: *m f t*, *m f t*, *m f t*, &c., the following effects are produced.

1. In the outermost *m* on the left, and the outermost *t* on the right, examination with the electrometer (not the galvanometer) shows the presence of a quantity of free positive and free negative electricity, which increases with the number of simple circuits united:—indeed, the free electricity appears to increase in direct proportion to the number of simple circuits.

2. When one of the external pieces of metal is connected with the ground, and its free electricity thereby removed, the quantity of the opposite free electricity in the other external piece of metal is doubled.

3. When the two outside pieces of metal are connected by means of a good conductor—*e. g.* a wire—and the *open circuit* thereby converted into a *closed circuit*, the deflection of a magnetic needle in the neighbourhood of the wire is very little, if at all, greater than that which would be produced by a simple circuit consisting of the same elements,—provided that, in the latter case, the connecting wire is thick enough to afford free passage to electricity of small tension.

4. But the tension of the current increases with the number of simple circuits connected together; and hence, the current generated by a compound circuit can pass, with little or no diminution of strength, through long wires and imperfect conductors, by which the current of a simple circuit would be greatly enfeebled, or even completely arrested.

5. If, while the circuit is closed, the contiguous pieces of metal *t*, *m*, be separated, and then connected by a wire, an electric current will pass through every such wire, of the same quantity and tension as that which

passes through the metallic arc connecting the two outermost pieces of metal.

[*Circuit open:* If two pairs of metallic plates—*e. g.* of zinc and copper —are placed in two cups or cells *a*, *b* (*App.* 23), filled with the same liquid, acidulated water for instance, C^1 being connected with Z^2 by a wire *g i*, but Z^1 not connected with C^2 by the wire *o p*,—the negative electricity set free by the oxidation of Z^2 may indeed pass over to C^1, and thence to the hydrogen set free by Z^1:—but since the negative electricity set free in Z^1 has no other way of escaping than by passing to the hydrogen of the cell *a*, and the hydrogen liberated in the cell *b* can only receive its negative electricity from Z^2,—scarcely anything but purely chemical action takes place, and the hydrogen is evolved on the two zinc plates. But just as in the unclosed simple circuit (p. 342, *c*), so likewise in this case, a feeble electro-chemical action takes place: for, in consequence of the difficulty which the negative electricity finds in passing from the zinc to the hydrogen, a small quantity of negative electricity—which may be called one negative portion—remains in Z^1 and Z^2. The small quantity of hydrogen which does not receive from the zinc the quantity of negative electricity belonging to it, either takes it from the caloric of the liquid and liberates positive electricity, which passes over to C^1 and C^2,—or it is conveyed by transposition from Z^1 to C^1, and from Z^2 to C^2, taking up negative electricity in both these plates, and liberating positive electricity (one positive portion (α) in each plate). The positive portion in C^1 immediately unites with the negative portion in Z^2 to form caloric (β); and since to the negative portion in Z^1, there is no longer opposed any positive portion in C^1, nor any negative portion in Z^2 to the positive portion in C^2, and consequently the electrical difference is reduced one-half,—it follows that 2 negative portions can accumulate in Z^1 and 2 positive portions in C^2, till the tendency of the two electricities to combine prevents their further accumulation. Upon this, a second positive position passes into C^1 and a second negative portion to Z^2 (γ); but these portions again neutralize one another (δ). Whereas, therefore, in the simple galvanic circuit, the zinc contains one negative portion and the copper one positive portion of free electricity,—in the two-pair circuit, on the other hand, Z^1 contains 2 negative portions and C^2 2 positive portions, while C^1 and Z^2 are neutral. This accumulation of a double quantity of negative electricity in Z^1 and of positive electricity in C^2, produces a twofold electrical tension.

	Z'	C'	Z^2	C^2
α	−	+	−	+
β	−	0	0	+
γ	2 −	+	−	2 +
δ	2 −	0	0	2 +

When three simple circuits are united (*App.* 24), one positive portion from C^1 is neutralized by one negative portion from Z^2, and similarly, one positive portion from C^2 by one negative portion from Z^3 (α, β): and since these 4 plates are thereby rendered neutral, a second negative portion can accumulate in Z^1 and a second positive portion in C^3—whereupon the portions developed in the 4 middle plates again neutralize one another, (γ, δ). But thirdly, 2 negative portions accumulate in Z^2, half of which is communicated to C^1, and 2 positive portions in C^2, half of which is communicated to Z^3 (ε, ζ). Since now Z^1, which already contains 2 negative portions, is opposed to C^1, with one negative portion, a third

negative portion can accumulate in Z^1, until the maximum is attained; —and in the same manner, 3 positive portions accumulate in C^2, which is opposed to Z^2, containing one positive portion (ϖ). Lastly, the portions in C^1 and Z^2, and those in C^2 and Z^3, distribute themselves uniformly (ϑ).

	Z^1	C^1	Z^2	C^2	Z^3	C^3
α	−	+	−	+	−	+
β	−	0	0	0	0	+
γ	2 −	+	−	+	−	2 +
δ	2 −	0	0	0	0	2 +
ε	2 −	0	2 −	2 +	0	2 +
ζ	2 −	−	−	+	+	2 +
η	3 −	0	2 −	2 +	0	3 +
ϑ	3 −	−	−	+	+	3 +

According to this, the portions of electricity are distributed as follows in an unclosed circuit:—Simple Circuit: Z —, C +. Two-pair Circuit: Z^1 2 —, C^1 0, Z^2 0, C^2 2 +. Three-pair Circuit: Z^1 3 —, C^1 —, Z^2 —, C^2 +, Z^3 +, C^3 3 +. Four-pair Circuit: Z^1 4 —, C^1 2 —, Z^2 2 —, C^2 0, Z^3 0, C^3 2 +, Z^4 2 +, C^4 4 +. Five-pair Circuit: Z^1 5 —, C^1 3 —, Z^2 3 —, C^2 —, Z^3 —, C^3 +, Z^4 +, C^4 3 +, Z^5 3 +, C^5 5 +, and so on. Hence the quantities of electricity accumulated in the terminal plates,—and, therefore, also the electrical tensions of the poles,—increase in direct proportion to the number of plates.

When one of the terminal plates is connected with the ground, *e. g.* C^2 of the double circuit (*App.* 23), and the two portions of positive electricity thereby conducted away, a fresh accumulation of elrctricity takes place in the opposite terminal plate to the same amount as before, making in all 4 negative portions. For since C^2 is neutral, 2 negative portions can accumulate in Z^2, till the maximum of tension is attained, and similarly in C^1, which is connected with it; so that Z^1 opposite to C^1 can now retain 4 negative portions. In the same manner, 4 positive portions accumulate in C^2 when the electricity of Z^1 is conducted away. Generally; whatever may be the number of pairs in the battery, the electrical tension of either pole is doubled when the electricity accumulated in the other pole is conducted away.]

[*Circuit closed:* As soon as Z^1 is connected with C^2 (*App.* 23) by a metallic arc *o p*, electro-chemical action is enabled to proceed on an extended scale. The negative electricity developed by the oxidation of Z^1 goes through *o p* to C^2, and thence to the hydrogen liberated by Z^2 from the water in cell *b*. The negative electricity evolved at the same time from Z^2 passes through C^1 to the hydrogen, which is transferred from Z^1 to C^1. Hereupon, negative electricity goes from *o* to *p* and from *i* to *g*,—or, what comes to the same thing, positive electricity goes from *p* to *o* and from *g* to *i*.

The quantities of electricity flowing through *o p* and *g i* are equal: the galvanometer shows the same deflection, whether it is interposed between *o p* or *g i*. This is in accordance with the fact, that the quantity of hydrogen gas evolved on C^1 is the same as that on C^2. Suppose, for example, that the electro-chemical action were stronger on Z^1 than on Z^2: the quantity of negative electricity transmitted from Z^1 to C^2 would then be more than sufficient to saturate the hydrogen gas there evolved, while Z^2 would give to C^1 a quantity of negative electricity less than that required by the hydrogen evolved on C^1. Hence the electro-chemical actions in the two cells control one another in such a manner, that equal

quantities of electricity pass through the two metallic arcs, and equal volumes of hydrogen gas are evolved on the two copper plates. If the chemical action in one cell becomes stronger than that in the other, the excess takes the purely chemical form, and the superabundant hydrogen is all evolved upon the zinc.

The current which passes from *o* to *p* in a two-pair circuit is not greater in quantity than that which traverses the connecting wire of a simple circuit; provided that the quantity of zinc dissolved off the zinc plate of the latter in a given time is equal to that dissolved from each zinc plate of the two-pair circuit, and that no purely chemical action takes place in either case (as when amalgamated zinc is used);—or else that in both cases the quantity of purely chemical action bears the same proportion to that of the electro-chemical action. For the negative electricity which in the two-pair battery runs through *o p*, proceeds, not from both zinc plates, but only from Z^1; and if no more of this plate be oxidized in a given time than of the zinc plate of a single pair, the quantity of negative electricity developed in the former case will likewise not be greater than that developed in the latter. The negative electricity evolved from Z^2 merely passes through the arc *g i*, and is absorbed at C^1 by the hydrogen. Similarly, with batteries consisting of several pairs;—so many pairs, so many separate currents.

If the circuit be opened at *g i* while it remains closed at *o p*, C^1 and Z^2 become the poles. If, therefore, in a battery consisting of several pairs, and having its ends metallically connected, any zinc plate be separated from the copper plate with which it is associated, those two plates become the poles.

The quantity of electricity in the current may however be increased by augmenting the number of pairs, if the electro-chemical action in the individual pairs is accompanied by purely chemical action. For, the greater tension or velocity of the current produced by several pairs causes the purely chemical action to diminish and the electro-chemical action to increase. But this increase of quantity can only rise to the maximum at which the action becomes wholly electro-chemical—and consequently, all the negative electricity of the zinc passes to the hydrogen through the other metal.

It appears then that the union of several pairs in a battery increases the tension of the electric current in direct proportion to the number of pairs,—and likewise augments the quantity to a certain extent in those cases in which a considerable quantity of the negative electricity of the zinc in the simple circuit is withdrawn from the current by purely chemical action.

We may conclude then that the *Quantity* of the electric current of a galvanic battery depends: 1. On the strength of the electro-chemical action in the individual simple circuits of which the battery is composed—principally therefore on the circumstances considered (pp. 376....381.) 2. On the number of pairs—because as that number is increased, pure chemical action is more and more prevented.

The *Tension* depends: 1. On the tension of a simple circuit: and 2. On the number of simple circuits conjoined.

According to the view just laid down, a galvanic battery of zinc and copper with fluid, should be constructed in the following order: $Z f C$, $Z f C$, $Z f C$, &c.; and accordingly, the zinc pole is negative and the copper positive, as in the simple circuit. But according to the contact theory, which regards the contact of the two metals as the principal source of the

electricity, the battery should be arranged as follows, C Z *f*, C Z *f*, C Z *f*, &c. In this arrangement, the copper pole on the left is negative and the zinc pole on the right positive. Hence, the expressions, *copper pole* instead of negative pole—and *zinc pole* instead of positive pole, are of frequent occurrence. But according to the chemical theory, the outermost copper on the left and the outermost zinc on the right are altogether without influence on the force of the battery; and if these two external members are removed, the first mentioned arrangement remains behind.]

Ohm's Formulæ, relating to the Quantity of the Electric Current.

1. *For a conductor into whose extremities the two electricities flow with a given tension:*

Let A be the electrical tension; K the conducting power of the wire or other conductor; *w* the surface of its transverse section; L its length; Q the quantity of the current, then

$$Q = \frac{A\,K\,w}{L}$$

Hence the quantity of the entering electricities which pass through the wire in a given time, varies directly as the tension of the electricities, the conducting power and thickness of the conductor,—and inversely as its length. Hence also, the quantity of the current in two conductors is the same, when, with equal electrical tension and conducting power, the ratio of the transverse section to the length is the same in both; or, with equal tension and equal transverse section, the ratio of the conducting power to the length is the same; or, with equal conducting power and equal transverse section, the ratio of the tension to the length is the same.

2. *For a simple Galvanic circuit.*

Let A be the electromotive power of the circuit (or the tension i), R the resistance which the current meets with in the circuit itself. This is the resultant of the following individual resistances:—*a*. Resistance of the two metallic plates which the current has to traverse;—*b*. Resistance of the liquid through which, according to the ordinary view, the current passes, [according to p. 343, *f*, this is the resistance which the liquid opposes to the transposition of atoms]. To this, Fechner and Poggendorff add *c*): the resistance of transition,—*i. e.* the resistance which exists to the passage of the electric current from the metal to the liquid, and conversely.

Also, let *r* be the resistance of the conductor which unites the two metals, and Q the quantity of the electric current which enters it; then

$$Q = \frac{A}{R + r}; \quad \text{therefore } A = Q\,(R + r)$$

3. *For the Galvanic Battery.*

n denoting the number of united simple circuits,

$$Q = \frac{n\,A}{n\,R + r}$$

When the resistance *r* of the conductor which closes the circuit is

inconsiderable in comparison with the resistance R in the individual circuits, it nearly vanishes in the formula, and there remains

$$Q = \frac{n\,A}{n\,R} = \frac{A}{R}$$

that is to say: the quantity of the current is the same, whether it proceeds from one pair or from several.

But if the resistance of the conductor which closes the circuit is considerable—*e. g.*, from the interposition of water, &c.—then, Q increases considerably with the number of pairs—because then $\frac{A}{R + r}$ gives a much smaller quotient than $\frac{n\,A}{n\,R + r}$

The development of this subject may be found in Ohm's Memoirs already cited on page 307; likewise in *Ohm's Galvanische Kette*, Berlin, 1827; Fechner, *Maassbestimmungen der galvanischen Kette*, Leipzig, 1831; Pouillet (*Pogg.* 42, 281); Henrici (*Pogg.* 53, 277).

Quantity of the Electric Current of a Galvanic Battery.

With amalgamated zinc and platinum in dilute sulphuric acid, the quantity of the current is not increased by augmenting the number of pairs. One pair, by the oxidation of one atom of zinc—provided the connecting wire be thick enough to transmit the feeble current without diminution—supplies as much electricity in the form of a current, as 1000 pairs would supply by the oxidation of 1000 atoms of zinc. In all the cells, equal quantities of water are decomposed and equivalent quantities of zinc dissolved, viz. 32·5 parts (1 At.) of zinc, to 1 part (1 At.) of hydrogen gas evolved. (Faraday.)

A number of pairs does not produce a stronger deflection of the galvanometer than a single pair; one pair acts more, another less strongly. The sum of the effects [quantities] of the single pairs divided by the number of pairs gives the effect [quantity] of the pile: hence, a larger pair added to a number of smaller pairs increases the action,—a smaller pair diminishes it. (Marianini.)

Even though the several pairs, from differences in extent of surface or in the nature of the liquid, should individually produce different quantities of electricity,—still, all the currents which pass from the electro-negative to the electro-positive metals of the several pairs, after the union of these pairs, are mathematically equal. The quantity of electricity in the current of a battery is greater than that of the weakest pair taken singly,—because, when this pair is joined to the battery, no more pure chemical action takes place in it. A very feeble pair is to be regarded only as an interposed plate (*vid.* seq.) which weakens the current; and the quantity of the current remains the same, even when the weak pair is introduced in the reverse order. (De la Rive.)

The quantity of the current of a pile charged with dilute sulphuric acid is very much diminished, when this pile is united in the proper order with another containing only water. (Schönbein.)

If 10 pairs of amalgamated zinc plates and platinum plates are separately immersed in dilute sulphuric acid, different quantities of hydrogen gas are evolved in a given time on the surfaces of the several platinum plates, the variation amounting to about $\frac{1}{3}$ of the whole. But when all the 10 pairs are united into a battery, the quantity of gas evolved on

each platinum plate is the same, and equal to that which was before evolved on the platinum plate of the weakest pair. If the rings of all the zinc and platinum plates are immersed in a vessel filled with mercury, the development of gas on the platinum plates again becomes as unequal as in the first case. If every two zinc plates be connected with every two platinum plates, and the 5 double pairs united into a battery, the evolution of gas is the same in all the cells. When 8 pairs are left simple, and connected with one double pair to form a battery, the quantity of gas evolved on the two platinum plates of the double pair taken together, is not greater than that evolved on each platinum plate of the single pairs. When each of the 10 zinc plates is placed between two platinum plates, the evolution of gas on each double plate is increased nearly two-fold; and part of the gas likewise escapes on that surface of the platinum which is turned away from the zinc. When unamalgamated zinc is used, a great deal of hydrogen gas is evolved upon its surface; but the quantity evolved on the platinum is the same as when the zinc is amalgamated; hence the local [pure chemical] action does not interfere with the force of the current. (Daniell.)

If several pairs of amalgamated zinc and platinum in dilute sulphuric acid are united into a battery, and the polar wires dipped into dilute sulphuric acid, the quantity of hydrogen gas evolved in each exciting cell of the battery is exactly the same as that set free in the decomposing cell. When the circuit is imperfectly closed by the interposition of a long thin wire or a liquid conductor, the quantity of gas evolved in all the cells is diminished, but is the same in all; the greater the number of pairs, the less does this diminution in the quantity of hydrogen gas amount to. (Matteucci.)

Twenty pairs of zinc and copper give the same deflection of 20° as one pair, when the circuit is closed by a wire of sufficient thickness. But when the current is conducted from the poles through a stratum of water, the deflection with one pair amounts to 10°, with 5 pairs to 15·3°, and with 20 pairs to 19°. (Buff.)

One pair of plates gives the same deflection, whether the metals are separated by one or five pieces of cloth saturated with liquid; but when several pairs are united, the deflection diminishes as the thickness of the cloth is increased. The diminution is less however in proportion as the liquid conducts better [*i. e.*, exerts chemical action]. Marianini.

The following experiments by Binks were made with amalgamated zinc plates and platinum plates of equal size in dilute sulphuric acid.

The quantity of zinc dissolved in a given time diminishes as the number of plates is increased, in the following proportion—the first number denoting the number of pairs of plates, the second the loss of zinc: 1 : 5·7,—2 : 3·9;—4 : 3·8,—8 : 3·8,—16 : 3·4,—32 : 3·6,—40 : 3·8,—48 : 2·7.

A similar diminution takes place in the quantity of hydrogen gas evolved, when two pairs of unequal surface are united: *a* denotes the surface of each of the pairs of the plates, *b* the quantity of hydrogen gas which each would have developed by itself, *c* the quantity evolved after their union:

a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
1	0·8	0·4	1	2·4	2·4	1	3·2	4·4	1	1·4	2·6	1	0·8	1·6
1	0·8	0·4	3	7·4	2·4	5	16·0	4·4	9	12·0	3·6	16	12·8	2·6
Sum	1·6	0·8		9·8	4·8		19·2	8·8		13·4	6·2		13·6	4·2

It is remarkable that when the surfaces of the two pairs of plates are very unequal, the quantity of hydrogen evolved on the copper of the larger pair is greater than that evolved on the copper of the smaller. (Binks.)

The electric current of a battery ceases when the whole is cooled to — 18° [in consequence of the freezing of the liquid?]; it increases with the temperature, but ceases again at 100°, and recommences with violence on subsequent cooling. It is however considerably increased by heating only half of the battery to 100° (Dessaignes, *Ann. Chim. Phys.* 24, 203), —[this deserves verification].—A battery which at 15° gives a current, capable, when conducted through a watery liquid, of disengaging 22½ measures of hydrogen gas in a given time, yields 39 measures in the same time, when heated to 52°. (Despretz, *Gilb.* 72, 310.)

When the current of a trough-battery has diminished, it may be increased almost double by stirring the acid liquid between the zinc and copper plates with a feather. (Faraday.)

Electrical Tension of the Battery.

The tension of the unclosed circuit, as determined by the electrometer, increases directly as the number of pairs. (Volta, Bohnenberger (*Gilb.* 57, 346), Singer, Marianini.) It increases as the square of the number of pairs. (Delezennes, *J. Phys.* 82, 269). In the unclosed circuit, it increases as the square of the number of pairs, and in the closed circuit directly as the number; for the statical effects of a given quantity of electricity, as shown in the open circuit by the electrometer, are to the dynamical effects which the galvanometer exhibits in the closed circuit, in the ratio of the square to the simple number. (Peltier.)

The tension, as shown by the electrometer in the unclosed circuit is not affected by the size of the plates, but only by their number. When one pole is connected with the ground, the maximum of tension is the same, whether the battery be charged with river-water, solution of sulphuret of soda, or water acidulated with nitric acid; but in the last case, the maximum tension is instantly attained, more slowly in the second, and most slowly of all in the first. When the battery is insulated, the tension is altogether weaker,—strongest however when the charge is made with river-water, weakest when water acidulated with nitric acid is used: in the latter case, it often vanishes altogether. (De la Rive.) In the unclosed circuit, the nitric acid exerts an oxidizing action, not only on the zinc, but likewise on the copper, thereby giving rise to an opposite current; but when the circut is closed, the oxidation of the copper ceases. (Buff.)

The middle pair of an unclosed circuit of twenty pairs of zinc and copper does not act more strongly on an electrometer furnished with a condenser, than one single pair would. The greater the number of pairs included in the circuit by touching one of them with the condenser and the other with the finger, the stronger is the divergence of the gold leaves. Likewise, when the circuit is closed, but in such a manner that the current is obliged to pass through water—not decomposing it perceptibly—a certain degree of tension is manifest, increasing towards the poles. Even when dilute sulphuric acid is used instead of water, tension is still apparent, although the liquid is decomposed; but not when the circuit is completely closed by a metallic conductor. Whenever, therefore, an obstacle, such as water, is to be overcome, electricity accumulates in the poles till it acquires sufficient tension to overcome the resistance. (Buff.)

If the union of the electricities collected in the poles has been effected by connecting the poles by a perfect conductor, and the connection is afterwards broken, the two electricities again accumulate in the poles with their former tension. In piles with moist semi-conductors, this effect takes place almost instantaneously; in those with dry semi-conductors, often very slowly. So long as the poles remain connected by a good conductor, the positive and negative electricities rapidly generated in the battery continually recombine within the conductor. The quantity of electricity thus neutralized in a given time depends on the circumstances above noticed.

The difference between the effects of the voltaic pile and those of the electrical machine consists in the two following points: 1. By means of the latter, a large quantity of electricity may easily be accumulated in a body of small dimensions; in consequence of which, the electricity acquires a high tension or a strong tendency to combine with electricity of the opposite kind, and makes its way through non-conductors, such as the air, in the form of a spark. On the other hand, the tension of the electricity developed by the contact of two metals is so extremely small, that, according to Children, it requires no fewer than 1250 zinc and copper plates to give such a tension to the electricity accumulated at the poles, as will enable it to pass in the form of a spark between two platinum wires terminating in points, placed at an interval not exceeding $\frac{1}{50}$ inch, and connected with the poles of the battery.—(2.) But a small voltaic battery generates in a given time a much greater quantity of electricity than a large electrical machine,—provided the electricities are conducted away as fast as they are generated. The electrical machine, therefore, is best adapted to the production of those effects which depend on great electrical tension, such as the penetration of air, glass, and other insulators; the voltaic battery, especially when large plates are used, is most efficacious in producing those effects which depend on the combination of large quantities of electricity in a given time,—*e. g.*, an elevated temperature in the conductors in which the combination takes place, and the decomposition of chemical compounds.

Since an increased number of plates augments, not the quantity, but only the intensity of the current, it follows that the number of pairs united in the battery ought to be different, according to the conducting power of the body through which the current has to pass. A greater number of pairs than that required for completely overcoming the resistance, is of no avail—and may even diminish the quantity of the current, if any among them act less powerfully than the rest. Hence a single pair is proper when the current has to pass through a thick wire only (as for magnetic action or for fusing), a small number of pairs when it has to traverse a long thin wire, a larger number when watery liquids are placed in the circuit, and a still larger number when the liquids are divided into separate portions by interposed plates. (De la Rive.)

The greater the number of pairs, the sooner does the action diminish; so that a battery of a small number of pairs is stronger after a time than one containing a large number. (De la Rive.)

Strongly acting pairs must not be united with such as act weakly, *e. g.*, zinc and copper with copper and platinum; or pairs acted upon by fresh acid with pairs subjected to the action of acid which has been used and is therefore saturated; neither should large pairs be united with small ones. The addition of pairs which act less powerfully [though it increases the tension] diminishes the quantity of the current considerably. If 40

pairs with fresh acid produce a current capable of liberating 8·4 cubic inches of detonating gas in a minute by the decomposition of water, the quantity obtained in the same time is reduced to 1·1 cubic inches when these 40 pairs with fresh acid are connected with 10 pairs acted upon by acid previously used. (Faraday.)

Materials of the Battery.

Zinc, either common or amalgamated, is almost always employed as the *positive metal* of the battery. But since common zinc is subject to ordinary chemical action, and likewise—on account of alloys mixed with it—to local galvanic action; and since these actions continue even while the circuit is open—a great deal of zinc and acid are uselessly consumed. By the use of amalgamated zinc, first introduced by Sturgeon, this loss is avoided. With this kind of zinc, however, the current is soon reduced to $\frac{1}{8}$ or $\frac{1}{10}$ of its original strength, because no gas is evolved on the zinc, and consequently the acid does not get well mixed; but on breaking contact for a while, the current regains its former power.—Rolled zinc plates are preferable to those of cast zinc, which are less pure. New plates act better than such as have been used two or three times, perhaps because the alloys come out more prominently as the surface dissolves, and thus give rise to local galvanic action. This deterioration of zinc plates by use soon reaches its limit in the case of rolled zinc; but with cast plates it goes on continually. The more smoothly the plates are rubbed, the better do they work. (Faraday.)

For the negative metal—copper, iron, lead, silver, platinized silver, platinum, graphite, charcoal, or peroxide of lead may be used.

In a battery of iron, platinum, and dilute sulphuric acid, only a small quantity of hydrogen gas is evolved upon the platinum; but if the iron plates used in this battery are united with zinc plates, nearly twice as much hydrogen is evolved upon the iron, as would be given off, if the same zinc plates were connected with platinum. Fresh iron plates, on the contrary, do not act more strongly than platinum. (Daniell.)

When the surface of the negative metal is twice as great as that of the positive, and a plate of the latter is interposed between two plates of the former, the quantity of the current is greatly increased (p. 380). (Hare, Faraday.) The quantity is also greater, the thinner the stratum of liquid between the zinc and the negative metal (p. 377). (Faraday.)

A peculiarly strong action is produced by silver or plated copper, on which platinum is precipitated. A rough surface is first imparted to the silver by treating it for a short time with strong nitric acid; it is then immersed in dilute sulphuric acid, to which a little chloride of platinum has been added, and connected with zinc immersed in dilute sulphuric acid contained in a porous tube, this tube dipping into the first-mentioned liquid. The platinum is precipitated on the silver in the form of a black powder. (Smee.)

Of carbonaceous substances, the most serviceable are plumbago and hard gas-coke; then porous coke and box-wood charcoal. These, however, soon lose their power, in consequence of becoming filled with hydrogen: but if the hydrogen be removed by immersing them in a solution of sulphate of copper, which likewise produces a precipitation of copper upon and within them, a powerful battery may be made with them. (Smee.)

A mixture of coal and coke, strongly ignited, forms a carbonaceous mass, which acts nearly as well as platinum, and is well adapted for use

on account of its tenacity. (Bunsen, *Ann. Pharm.* 38, 211.) (*Comp.* p. 392.)

For *liquids*, the following may be used: spring-water, aqueous solutions of common salt, sal-ammoniac, nitre, alum, sulphate of copper, bisulphate of potash, and other salts, aqueous ammonia or potash, and dilute sulphuric, hydrochloric, or nitric acid, or a mixture of dilute sulphuric and nitric acids.

Water gives a continuous current of small quantity and attacks the zinc but very little. With saline solutions, the current is at first abundant, but soon diminishes (p. 377). Sulphate of copper is the only salt that gives a more permanent current; it also acts without evolution of gas.

A mixture of water, sulphuric acid, and nitric acid (*e. g.*, 100 measures of water to 4·5 oil of vitriol and 4 nitric acid) possesses this advantage,—that it not only excites an intense and abundant current, but that neither hydrogen nor nitric oxide gas is evolved from it, because the hydrogen evolved from the water combines with the nitrogen set free from the nitric acid, and forms ammonia. (For Fyfe's experiments on the power of different circuits, *vid. Pogg.* 43, 228.)

When dilute sulphuric and nitric acid are used together, instead of dilute sulphuric acid alone, in a battery of ten pairs of amalgamated zinc and platinum, the quantity of the current (measured by the Voltameter) is nearly trebled, and the quantity of hydrogen gas evolved in the different cells is small and unequal; but in five minutes the current ceases almost entirely, and is but imperfectly restored by opening the circuit. When more nitric acid is added, the evolution of hydrogen ceases entirely in some cells, and almost wholly in others: the current is strengthened, but diminishes rapidly. If when the circuit has been closed for thirty hours, and the current has almost wholly ceased, the platinum plates be removed and replaced by new ones, the battery will again act as strongly as at first, but only for a short time. The platinum plates, which have become inactive, are not completely restored by ignition, polishing, or boiling with strong solution of potash; but they recover their activity entirely by boiling in nitric acid. For they are covered with zinc partly crystalline, partly of a warty texture,—the coating even extending, though in smaller quantity, to the side which is turned away from the zinc. The rapidity with which this coating is formed, increases with the quantity of zinc dissolved in the liquid; it is therefore greatest when unamalgamated zinc is used.—Every time the circuit is broken, the zinc deposited upon the platinum dissolves again, provided a sufficient quantity of free acid be present. When the acid liquid holds a quantity of copper in solution, that metal is first deposited on the platinum, and afterwards the zinc, but with less facility. But when a larger quantity of copper is contained in the liquid, the copper is precipitated on the amalgamated zinc, and causes an evolution of hydrogen upon it. The addition of nitric acid to the dilute sulphuric acid assists the action by diminishing the evolution of hydrogen gas on the platinum, inasmuch as it gives rise to the production of ammonia [by which however the acid is so much the more quickly saturated]. (Daniell.)

Remarkably powerful currents are produced by the proper combination of two metals with two liquids (p. 389).

With plates of given surface, the quantity of the current varies according to their nature and that of the liquid, as follows: Amalgamated zinc, dilute sulphuric acid, copper : 0·19;—amalgamated zinc, dilute sulphuric *acid, platinized* silver (according to Smee) : 0·29;—amalgamated zinc,

dilute sulphuric acid, iron (according to Sturgeon) : 0·30 or less;—zinc dilute sulphuric acid, sulphate of copper, copper (according to Daniell) : 0·65;—amalgamated zinc, dilute sulphuric acid, concentrated nitric acid, platinum (according to Grove): 1·09. (Joule.)

1. *Batteries with two Metals and two Liquids.*

Daniell's Constant Battery. (*App.* 25.) An ox-gullet closed at the bottom (or connected with a bent tube for carrying off the spent acid) contains dilute sulphuric acid and a rod of amalgamated zinc, and is fixed upright in a cylindrical copper vessel filled with a solution of sulphate of copper. The acid is either constantly renewed by causing it to flow into and through the bent tube, or occasionally by pouring it in when wanted. The solution of sulphate of copper is maintained at a constant strength by means of portions of the pulverized salt placed in sieves at the upper part of the liquid. From 10 to 20 simple circuits of this kind are united (the copper vessel of the first with the zinc cylinder of the second, the copper vessel of the second with the zinc cylinder of the third, and so on, the connection being made by metallic conductors).—This battery evolves no hydrogen gas, even when the ends are unconnected: the copper of the solution is gradually deposited, when the circuit is closed, on the inner surfaces of the copper cylinders. When the current is made to pass through acidulated water, the quantity of detonating gas evolved is greater in the first quarter of an hour than in any subsequent equal interval; but from that time the current remains perfectly uniform,—so that when the circuit has been closed for four hours, the quantity of detonating gas evolved in a given time on passing the current through acidulated water, is the same as before. The amount of pure chemical action in this battery is very small. For 188·48 cub. in. of detonating gas evolved in the decomposition of water by a ten-pair battery, 93·3 grains of zinc are dissolved in the same time from each zinc plate (therefore 933 gr. for the whole ten plates); that is to say, only 7·2 gr. more than the quantity required by the stoichiometrical proportion of water decomposed to zinc dissolved (9 : 32·2).—Whilst the ten-pair battery, when the zinc is immersed in a mixture of 100 measures of water and $4\frac{1}{2}$ measures of oil of vitriol, liberates 3 8 cub. in. of detonating gas in 5 minutes,—it gives 2·1 cub. in. when nitric acid is added to the sulphate of copper solution, and 4·2 cub. in. on the addition of nitric acid to the sulphuric: the latter quantity however soon sinks again to 3·8 cub. in. Hence the addition of nitric acid is useless. With a mixture of 100 measures of water and 9 measures of oil of vitriol, the quantity of gas obtained in 5 minutes is 5·5 cub. in.; and with 100 water and 12·5 oil of vitriol, it amounts to 11· cub. in.—When the circuit is kept closed for five hours without renewal of the acid, the quantity of detonating gas evolved in 5 minutes sinks from 2·7 to 2·4 cub. in., and after 24 hours to 0·3 cub. in.; the acid is then found to be completely saturated with oxide of zinc. If half the liquid be now replaced by fresh dilute sulphuric acid, the quantity of detonating gas evolved in 5 minutes rises, not merely to the original quantity of 2·7, but to 4·2 cub. in.; and the battery retains this strength for 4 hours, because the solution of sulphate of zinc mixed with the liquid increases its conducting power. The action remains the same when the zinc cylinders are reduced to one-fourth of their former length. The current is not increased when the copper surface is extended by the introduction of a number of slips of copper.—A twenty-pair battery

makes a platinum wire 8 inches long and $\frac{1}{100}$ of an inch thick, incandescent in the air.—If a zinc cylinder in one of the cells be replaced by a thick platinum wire, pure oxygen gas is evolved upon it, 84 cubic inches in an hour. (Daniell.)

Jacobi (*Electrotype, Petersburgh*, 1840) places a plate of lead or of thick copper rolled up into a cylinder (not soldered, in order that the precipitated copper may be removed by unbending it) in an oblong rectangular vessel of copper or lead. This cylinder touches three sides of the vessel. The space between it and the fourth side serves to receive a sieve-bottomed trough placed in its upper part and filled with pounded sulphate of copper, in order that the solution which drains through the bottom of the trough may supply the loss of that salt resulting from the galvanic action. Within the lead or copper cylinder is placed another cylinder made of the thinnest possible earthenware, filled with dilute sulphuric acid, and containing a zinc cylinder either solid or hollow. The liquid is withdrawn by means of siphons of peculiar construction; at all events, the acid liquid must be removed from time to time as it becomes saturated with zinc. The earthenware cylinders are soaked in water every six or fourteen days, in order to re-open their pores.

Instead of animal membranes, on which copper becomes precipitated, Mullins uses a hollow cylinder of sycamore or other white wood closed at the bottom; he also uses a solution of equal parts of water and saturated solution of sal-ammoniac in plate of dilute sulphuric acid. (For the other alterations, *vid. Phil. Mag. J.* 15, 37.)

Spencer (*Pogg.* 51, 372) substitutes for the ox-gullet in Daniell's battery a cylinder of thick brown packing paper, modelled upon a wooden cylinder, fastened with sealing wax throughout its whole length by means of a hot iron, and closed at bottom with a thin round plate of wood which has a circular groove cut in it, so that it may be tied with a string to the paper cylinder. Solution of Glauber's salt or sulphate of zinc is used instead of dilute sulphuric acid.

Or:—a glass cylinder outside; within this, a cylinder of thin sheet lead or the lead of which the Chinese tea-canisters are made, with numerous vertical folds, so that it has a starry appearance and presents a large surface. Within this again is placed a cylindrical vessel of unglazed earthenware; and this contains a cylinder of zinc surrounded with sulphate of soda or sulphate of zinc. The lead immersed in the solution of sulphate of copper soon becomes covered with copper, and acts like that metal.

Grove's Battery. (*App.* 26.) A porcelain trough is divided by partitions *s*, also of porcelain, into four cells, *a*, *b*, *c*, *d*. Each cell contains a box *i* of porous earthenware. Between the surfaces of the cell and the box is placed a platinum plate *p t*, passing downwards on one side of the cell and upwards on the other,—and in the earthenware box, an amalgamated zinc plate *z*, connected with the platinum plate of the second cell by thick wires screwed on to the zinc and the platinum, &c. The box *i* is filled with water containing one-fifth of its bulk of oil of vitriol, or one-half its bulk of hydrochloric acid; and the space containing the platinum is filled with a mixture of equal parts of oil of vitriol and strong nitric acid. The apparatus is fitted with a cover containing lime, in order to absorb the nitrous vapours which are evolved.—The apparatus contains eight ounces of liquid. It must not be left in action more than half an hour, because it becomes too hot. (Grove. *Vid.* p. 391.)

An instrument of this kind furnished with only single platinum plates —each of the four zinc and platinum plates having a surface of 14 square

inches, liberates 6 cubic inches of detonating gas per minute, when the connecting wires are made to dip into water acidulated with sulphuric acid,—brings a platinum of 7 inches long and $\frac{1}{10}$ of an inch thick to a state of bright ignition—and causes steel needles to burn with brilliancy. (Grove.)

A five-pair battery of this description having in each earthenware cell a platinum plate, 8 inches long and 2 inches wide, immersed in nitric acid of 1·35 sp. gr.,—and in each porcelain cell a zinc plate of double the size bent round at the bottom and immersed in hydrochloric acid—yields 15 cubic inches of detonating gas per minute, fuses platinum wire of the thickness of a knitting needle in a few seconds, causes charcoal to emit a light of intolerable brilliancy, and will produce a magnet capable of bearing 3½ cwt. Its physiological effects however are but slight [on account of the feeble tension of five pairs]. The current is likewise of constant strength. (Schönbein, *Pogg.* 49, 511.)

Porcelain cylinders, closed at bottom and covered on the outside with a layer of platinum burnt in, may be placed in cylinders of porous earthenware filled with nitric acid, and these again in vessels containing cylindrically bent zinc plates with dilute sulphuric acid, or still better, sulphate of zinc. (Pfaff, *Pogg.* 53, 303.)

Instead of platinum, an iron rod may also be immersed in strong nitric acid contained in a tube of gypsum, and the tube placed in a vessel containing dilute sulphuric acid, in which is immersed a zinc plate bent into the form of a cylinder. After this battery has acted for some time, the acid becomes so much weakened that it dissolves the iron suddenly. (Hawkins, *Phil. Mag. J.* 16, 115.—Poggendorff's Arrangement, *Pogg.* 54, 425.)

When the following carbonaceous substances are used instead of platinum in Grove's battery, the quantity of detonating gas evolved in a given time is found to diminish as follows:—Platinum: 3·52;—graphite: 3·4;—gas-coke, such as is deposited in the form of a hard crust in the retorts in which illuminating gas is generated: 3·27;—well burnt charcoal: 3·17. The action of all these substances is therefore nearly the same as that of platinum. (Cooper, *Phil. Mag. J.* 16, 35.)—Schönbein (*Pogg.* 49, 589) found the same result with gas-coke.—Charcoal having a surface of 8 square inches liberates as much gas as platinum 7 square inches in surface. (Smee.)

Bunsen (*Ann. Pharm.* 38, 311; *Pogg.* 54, 417) forms cells of carbonaceous substance prepared in the manner already described (p. 392), fills these cells with a mixture of sand and nitric acid, which is renewed from time to time as it is used up,—and places them in dilute sulphuric acid, also containing the zinc plates. A battery of three such pairs with zinc plates 3 inches wide and 4 inches long, liberates from 38 to 45 cubic centimetres of detonating gas per minute,—while, for every atom of water decomposed, not much more than one atom of zinc is dissolved in each cell. Platinum wires of some thickness are made red-hot, and charcoal brought to a state of dazzling incandescence. (*Vid.* Poggendorff, *Pogg.* 54, 419.)

Wöhler & Weber (*Ann. Pharm.* 38, 307) form two cylinders, open above and below, out of a piece of polished iron plate: one of the cylinders is made wider than the other, and the two are connected by a bent piece of metal. The wider cylinder is placed in a glass vessel containing dilute sulphuric acid,—in this is immersed an earthenware cylinder filled with strong nitric acid,—and in this, the narrower cylinder of the following pair. The iron in the sulphuric acid acts like zinc, that in the nitric acid

like platinum. When the surface of the wider cylinder is only three square inches, two pairs of this arrangement are sufficient to raise thin platinum wire to a white heat. Tinned plate appears to be preferable for immersion in the nitric acid; it is perhaps most advantageous to have the whole made of cast iron. (Wöhler.)

Three pairs of iron cylinders having a total surface of 12 square inches, three iron cylinders in nitric acid of 1·44 sp. gr. and the three others in a mixture of 7 parts water and 3 parts oil of vitriol, yield $\frac{1}{3}$ of a cubic inch of detonating gas per minute.—Five pairs of tin-plate (instead of zinc) and iron-plate (instead of platinum) having a total surface of 83 square inches, yield 1·8 cubic inches of detonating gas per minute, whereas an apparatus of zinc and platinum of the same size yields 9 cubic inches. (Walchner, *Ann. Pharm.* 40, 121.)

Aqueous solution of sesquichloride of iron in Grove's apparatus produces an action less by one fourth than that of nitric acid. (Smee.)

Grove's battery is stronger than any other of equal surface: its disadvantages are,—the great expense,—the inconvenience caused by nitrous fumes and the use of corrosive nitric acid,—and the mixing of the liquids by endosmose.

2. *Batteries with two Metals and one Liquid.*

A. *The negative metal having twice as much surface as the positive metal.*

Faraday, adopting Hare's method, makes two rectangular bends in the middle of a copper plate *k k* (*App.* 31), so that the sides run parallel to one another; he then solders the upper end of one-half of the plate to a zinc plate *z* by means of a bent piece of metal *b*,—and connects several such pairs in such a manner, that the zinc plate of the first shall be inserted between the two copper plates of the second, and kept from touching the copper by the introduction of small pieces of cork, $\frac{1}{10}$ of an inch thick,—the zinc plate of the second between the two copper plates of the third, and so on. The copper plates of one pair are kept from contact with those of the next by the insertion of thick paper. But as the paper becomes saturated with nitric acid, and this acid dissolves copper, which is subsequently precipitated on the zinc, it is better to separate the copper plates by strips of glass. The plates thus arranged are placed in the division *a* of the double trough represented in *App.* 32. Forty pairs require a trough 15 inches long, and 100 pairs a trough 3 feet long. The double trough is moveable round the axis *x*. A quarter revolution brings the trough *b* below and the trough *a* on the side, so that the acid liquid runs from *a* into *b*. Hence it is only necessary to turn the apparatus a quarter round, in order to bring the acid in contact with the plates or to discharge it; thus, all unnecessary action of the acid on the zinc is avoided. The intervals between the copper and zinc in this apparatus being much smaller than in the common trough battery, and the quantity of acid liquid employed being consequently much less, the liquid becomes more quickly saturated, and must be more frequently renewed. An apparatus of this description, containing forty pairs with a surface of three square inches, acts as strongly as an ordinary trough apparatus (with single copper surface) containing forty pairs, having a surface of four square inches. (Faraday.)

Sturgeon's Battery consists of eight cast-iron cylindrical vessels, 10 inches high and 3 inches in diameter: in each of them is placed an amalgamated zinc cylinder, connected with the next iron vessel by means of a

thick copper wire, to which it is soldered, and fixed into a wooden ring which prevents contact between the zinc and iron. The vessels contain a mixture of 8 parts water and 1 part oil of vitriol (a mixture which acts by itself on amalgamated zinc). The battery makes thick platinum wire red hot, yields from 4 to 5 cubic inches of detonating gas per minute, and, though not exactly constant, continues in action for a long time. (Mohr, *Pogg.* 51, 372.)—According to Sturgeon, the following batteries, each having ten pairs of plates, with a surface of 104 square inches, yield the following quantities of hydrogen gas per minute by the decomposition of water: Sturgeon's, 25; Grove's, 24; Smee's, 15; Daniell's, 12 cubic inches.

Children's Battery consists of forty copper and twenty zinc plates, each 6 feet long and 2 feet 8 inches wide, each zinc plate being placed between two copper plates (*Phil. Tr.* 1809, p. 32. *Schw.* 1, 374; 9, 212; 16, 359; also Gilb. 36, 334; 52, 353.)

Wollaston's Cell Apparatus. Zinc plates are immersed in long and deep, but narrow, copper cells, filled with an acid liquid. The first cell is connected by a semicircular strip of metal with the zinc plate which dips into the second cell, and so on. (*Compare* Hart, *Ed. J. of Sc.* 4, 19.)—The apparatus of the Florentine Museum consists of six zinc plates, each 85 inches square, immersed in six copper cells. (*N. Tr.* 6, 1, 219.)—If the cells are made of platinized silver or platinized plated copper (p. 419), and contain a mixture of 1 measure of oil of vitriol with 8 measures of water in which zinc plates are immersed, the battery acts very strongly, and will continue in action for forty-eight hours without requiring fresh acid. (Smee.)

De la Rue (*Phil. Mag. J.* 9, 484; 10, 244) fills the copper cells with solution of sulphate of copper, and places an amalgamated zinc plate in each (an unamalgamated zinc plate would become covered with copper). The action is stronger than with acids, and no gas is evolved.

Young's Battery (*Phil. Mag. J.* 10, 241; also *Pogg.* 40, 625), in which two connected zinc plates are interposed between two connected copper plates, in such a manner that one of the zinc plates is placed between the two copper plates, and one of the copper plates between the two zinc plates, does not possess any particular advantage.

B. *The surface of the negative metal not greater than that of the positive metal.*

Simple Trough or Cell-Apparatus. Oblong troughs of earthenware are divided into cells by earthenware partitions. Each cell contains a pair of plates of the two metals not in contact with each other; the positive plate of the first cell is connected by a curved strip of metal with the negative plate of the second cell, &c., &c. All the cells contain the same liquid.—The number of pairs used in this kind of battery is, for the most part, greater than in those previously described; hence the tension is greater; but the quantity, unless very large plates are used, is smaller.

The battery of the Royal Institution of London consists of 2000 pairs of plates, each plate having a surface of 32 square inches on one side. At the *École Polytechnique*, in Paris, there is a trough battery of 600 pairs of plates, each plate having a surface of 11 square inches. (Gay-Lussac & Thenard, *Recherches*, 1, 1.)

In the *Cup-apparatus* (*Couronne des tasses*) a number of copper wires bent knee-shape, and each having a ball of zinc fused on to one of its ex-

tremities, are immersed in a series of glasses containing dilute acid, in such a manner, that the zinc end of each wire dips into one glass and the copper end into the next. The action is but slight, on account of the small surface of the metals.

If twenty-four bent iron wires be covered at one end with peroxide of lead (by precipitation in the voltaic circle), and their ends made to dip into twenty-four glasses containing 1 part of nitric acid in 100 parts of water, each glass containing the clean end of one wire and the coated end of another, a battery is obtained which gives slight shocks, but loses its power as the peroxide of lead dissolves. (Schönbein.)—An apparatus of twelve platinum and twelve passive iron wires, immersed in nitric acid of sp. gr. 1·35, produces a very feeble current, which scarcely decomposes iodide of potassium, and has no effect on sulphate of copper or acidulated water. (Schönbein.)

In the *Voltaic Pile*, properly so called, the pairs of plates are disposed in alternate horizontal layers, with pasteboard, woollen cloth, or felt, saturated with a saline solution of dilute acid, &c. It acts like the trough-battery, but evolves less electricity in a given time, because the contact of the liquid with the metals is less complete.

Instead of plates of copper, Straub (*Schweiz. naturw. Anzeiger, Jahrg.* 4, S. 7,) recommends layers of carbonaceous matter. To prepare these, 7 parts of beech-wood charcoal, in fine powder, are mixed with 4½ parts of wheat-flour, and a proper quantity of water, into a paste; the paste is then moulded by pressure into flat circular pieces; and these, after being dried in sand in the open air, are exposed for three or four days to a continually increasing heat, till they smell like burnt bread. They are then ground quite smooth upon sand-stone, ignited between charcoal powder, and ground again. Before using them, they are soaked in water; after use, they are steeped in dilute hydrochloric acid to free them from zinc, and then washed.

De Luc's or *Zamboni's Pile.* The so-called *Dry Pile* is usually formed of thin sheets of metal separated by paper,—*e. g.*, of discs of so-called gold and silver paper, joined together by their paper surfaces—or of silver paper having its paper side smeared with honey, and then sprinkled with peroxide of manganese. Since the number of plates in these piles can easily be raised to several thousands, the poles exhibit sufficient tension to give sparks. But the quantity of the electric current, which can arise from nothing but the chemical action of the hygroscopic water in the paper on the tin of the so-called silver paper, is extremely small. Hence the poles, after being discharged, take a long time to recover their former tension; the pile produces no ignition of metallic wires, and does not readily exhibit chemical action. It was only by employing plates of greater size than those generally used, that Bohnenberger obtained a slight decomposition of water.—The pile when perfectly dry gives no more electricity (Parrot, H. Davy), and the quantity which it yields is greater in proportion to the quantity of moisture which it contains. (Parrot.) If the pile be dried by surrounding it with chloride of calcium, and raising its temperature, it will afterwards exhibit no electricity at ordinary temperatures, but will become electrical when heated. At temperatures between 70° and 75°, the tension of the poles is even greater than in an undried pile at ordinary temperatures. But when the poles have been discharged, the accumulation of electricity in the dried pile is much slower than in one which has not been perfectly dried. (Jäger.)

In the undried pile also, the tension of the poles is increased by heat-

ing to 24°; the application of a stronger heat produces no perceptible increase of tension. In vacuo, the pile exhibits the same tension as in the air. If the positive pole be connected with the conductor of an electrical machine, the negative electricity of the opposite pole sinks to 0; but when the negative pole is connected with the conductor, the tension of the positive pole increases. (Donné.) After the lapse of some time, the tin of the silver paper becomes dull and tarnished (H. Davy), and the pile gradually loses the whole of its power. (Jäger.)

Comp. Zamboni (*Gilb.* 60, 151); Heinrich, Schübler, Schweigger (*Schw.* 15, 113, 126, 132); Jäger (*Gilb.* 62, 227); Donné (*Ann. Chim. Phys.* 42, 71,—abstr. *Schw.* 58, 81); Rosenchöld (*Pogg.* 43, 193, and 440.)

3. *Batteries consisting of one Metal and one Liquid.*

If square pieces with long tails be cut out of zinc or tin-foil, and placed in about thirty watch-glasses filled with water, and arranged near one another, so that a square may lie in one watch-glass and the strip attached to it in the next,—and consequently each watch-glass, excepting the first and last may contain a square and a strip belonging to two different pieces of metal,—the arrangement thus produced will be *Zamboni's Pile of two Elements.* In such a case, according to Zamboni, the first watch-glass into which the first square dips, or the pole towards which all the squares are directed, is negative,—and the last watch-glass into which the last strip dips, or the pole towards which all the strips are directed, positive. With copper-foil, the opposite arrangement of the poles takes place. [According to this, the piece of zinc or tin of greater surface must be negative towards that of smaller surface, and the contrary with copper.] But, according to Erman, the positive pole in the zinc-foil arrangement is that towards which the squares are directed, and the negative pole that towards which all the points are directed; the contrary with silver. According to Erman, also, the current continues for two days only at the utmost, and may then be reproduced for a shorter time by the addition of common salt to the water.

If pieces of so-called gold-paper (or silver-paper) be formed into a pile, the metallic pole of this pile is positive, the paper pole negative. (Erman.) [Is the surface of the metal which is turned towards the paper less smooth than the outer surface?]

If eighty zinc plates, 4 square inches in surface, polished on one side and rough on the other, be placed in a wooden trough at the distance of 1 or 2 millimetres from one another, so that they may be separated by thin strata of air, and one pole of this pile be connected with the electroscope, the other with the ground,—the electroscope receives a considerable charge. The two surfaces of the zinc, being of different degrees of smoothness, act like two metals, and the film of air supplies the place of a liquid. (Watkins, *Pogg.* 14, 386.) [This deserves verification.]

On filling a number of copper vessels, 1, 2, 3, 4, 5, 6, 7, 8, with dilute sulphuric acid, connecting 1 with 2, 3 with 4, 5 with 6, and 7 with 8, by means of brass wires,—on the other hand, 2 with 3, 4 with 5, and 6 with 7, by means of bundles of thread saturated with salt-water,—and heating only the vessels 1, 3, 5, and 7,—a current is produced, sufficient, when fourteen vessels are used, to decompose water, if the electricity be conducted through that liquid by means of brass wires. As the heated vessels cool, the current ceases. (Schweigger, *N. Gehl.* 9, 704.)

4. *Batteries consisting of one Metal and two or three Liquids.*

If a number of U-tubes (*App.* 5) be filled on one side with concentrated, on the other with dilute sulphuric or nitric acid, and connected by arcs of the same metal dipping into the liquids—*e. g.*, tin, lead, iron, copper, or silver—an efficient battery is obtained. With sulphuric acid and iron, positive electricity goes from the end of the arc which dips into the dilute acid to that which dips into the strong acid; the contrary with tin and sulphuric acid. (Faraday, p. 400.)

If one end of the copper arc be immersed in solution of liver of sulphur, the other in dilute sulphuric acid, the solution of liver of sulphur being connected with the acid by a film of solution of common salt, a powerful battery is produced. (H. Davy.)

In a pile consisting of the following elements—cloth saturated with water, plate of metal (lead, copper, or silver plates answer best), cloth soaked in solution of liver of sulphur, cloth soaked in water, plate of metal, &c.—positive electricity goes through the metallic arc from the last element to the first. (H. Davy.)

5. *Grove's Gas Battery.*

¶ This battery consists of a series of tubes, containing strips of platinum foil covered with a pulverulent deposit of the same metal. The tubes are arranged in pairs in separate vessels of dilute sulphuric acid; and of each pair, one tube is charged with oxygen and the other with hydrogen gas, in quantities such as to allow the platinum to project above the dilute acid into the atmosphere of gas in the upper part of the tube. The platinum in the oxygen of one pair is metallically connected with the platinum in the hydrogen of the next; and thus a series may be composed of any number of pairs.—A battery of four cells constructed in this manner will decompose acidulated water; a single cell will decompose iodide of potassium; and twenty pairs will produce very powerful effects,—such as giving a shock which may be felt by several persons at once, producing a brilliant light between charcoal points, &c. When the poles are unconnected, a gold-leaf electroscope connected with either of them is sensibly deflected. When distilled water is substituted for acidulated water in the cells of the battery, the effects are similar but more feeble.

The current of positive electricity proceeds, *within the battery*, from the hydrogen tube to the oxygen tube *in the same pair*,—so that *in the voltameter*, the platinum connected with the terminal oxygen tube of the battery becomes the positive pole or *anode* (*vid.* Electrolysis, p. 431). In fact, the hydrogen in the battery tubes is the oxidable body, acting like the zinc in the ordinary battery. Both gases in the battery tubes are absorbed,—but the hydrogen twice as fast as the oxygen. It is essential that the platinum plates be immersed in the gases as well as in the liquid: for when these plates are made so short as not to project above the liquid, no action takes place. The use of the finely divided platinum is, of course, to increase the surface of contact. The rationale of the action appears to be as follows: "When the circuit is completed—at each point of contact of oxygen, water, and platinum, a molecule of hydrogen leaves its associated molecule of oxygen to unite with a molecule of the free gas; the oxygen thus thrown off unites with the hydrogen of the adjoining molecule of water; and so on,—till the last molecule of oxygen unites with a molecule of free hydrogen:—or we may conversely assume that the action commences in the hydrogen tube."

Mr. Grove likewise tried various other combinations of gases, viz. chlorine and hydrogen, chlorine and carbonic oxide, oxygen and nitrous oxide, oxygen and nitric oxide, hydrogen and carbonic oxide, &c.; but none of them were found to be adapted for actual use in the battery. Chlorine and hydrogen gave a powerful current; but the rapid absorption of the chlorine soon put a stop to the action. Chlorine and oxygen, on the one side, and hydrogen and carbonic oxide, on the other, were the only gases which appeared to be decidedly capable of combining electro-synthetically, so as to produce a voltaic current. The other combinations produced no effect, excepting for the first few minutes. Olefiant gas should perhaps be excepted: it appears to give a continuous but feeble current. The vapours of bromine and iodine, were they less soluble, would probably also be found efficient as electro-negative gases. (*Phil. Mag. J.* 21, 417; 24, 268, 346 and 422.) ¶

I. *Electricity developed by the Vital Process.*

Certain fishes, as *Torpedo unimaculata, marmorata, Galvanii* (the Electric Eel), and *Narke* (the Electric Ray); *Silurus electricus; Tetraodon electricus,* and *Gymnotus electricus,* have the power of constantly generating the two electricities in their bodies, in large quantity and of considerable tension, and imparting electric shocks.—In the Electric Ray, negative electricity proceeds from the under, positive electricity from the upper surface of the body. The electricity, when conducted away by wires, acts upon the magnetic needle, and decomposes liquids. (J. Davy.) Sparks may also be obtained from the Electric Ray by means of a peculiar apparatus. (Linari & Matteucci.) *Comp.* Humboldt (*Ann. Chim. Phys.* 11, 415); J. Davy (*Phil. Trans.* 1829, 15; also *Schw.* 57, 17; also *Pogg.* 16, 311;—*Phil. Trans.* 1832, 259; also *Pogg.* 27, 542); Linari & Matteucci (*Pogg.* 38, 292); Matteucci (*Pogg.* 39, 485); Linari (*Pogg.* 40, 642); Colladon (*Pogg.* 39, 411).

¶ Faraday has examined the electric force of the Gymnotus. He finds that the shock is strongest when one hand is applied to the head and the other to the tail,—and diminishes in force as the points of contact are brought closer together. The galvanometer was affected, and iodide of potassium decomposed—in such a manner as to show that the current proceeds from the anterior towards the posterior part of the fish. The spark was also obtained by means of a magneto-electric coil. When the shock was strong, it was like that of a large Leyden battery charged to a low degree, or that of a voltaic battery of perhaps one hundred and forty or more pairs, of which the circuit is completed for a minute only. (*Phil. Trans.* 1839, I, 1; *Phil. Mag. J.* 14, 211.)

The spark had previously been obtained from a gymnotus by Fahlberg and Guisan. (*De Gymnoto electrico,* Tubingen, 1819.) ¶.

II. Influence of Electricity on the Chemical Nature of Ponderable Substances.

1. *Combinations brought about by Electrical Influence.*

The combination of the two electricities often causes combustible bodies, which may be present at the place of combination, to unite with oxygen, chlorine, &c.

To this class of effects belong the inflammation of a mixture of oxygen with hydrogen or other combustible gases, or of chlorine with hydrogen, by the simple electric spark; of alcohol, ether, colophony, and gunpowder by slight electric discharges or by the simple spark; the burning of various metals in the form of thin wire or foil, when the combination of the two electricities takes place within their substance, and of charcoal by strong electric shocks or by the galvanic battery; and the combination of nitrogen with oxygen, when electric sparks are made to pass for a long time through a mixture of those two gases. According to Faraday, large electric sparks passed over litmus paper produce nitric acid sufficient to redden it.

In most of these cases, electricity appears to act by the development of heat which accompanies the union of its two kinds: it must, however, act in a different manner in the combination of oxygen and nitrogen, since this combination is not effected by heat. In this case, as in the inflammation of hydrogen by a small electric spark, the compression which the gases sustain in the passage of the spark must also be taken into account.

2. *Decompositions produced by the action of Electricity.*

When the two electricities are made to enter a compound body, either solid, liquid, or gaseous, which is not a perfect conductor, the compound is frequently resolved into its elements.

A. Decompositions produced by repeated Electric Discharges.

When the combining electricities are endued with high intensity, and their union takes place in the form of a succession of sparks in a compound gas or a compound solid body, decomposition of the compound often takes place. This effect may in some cases be due to the high temperature produced by the electric discharge, since many of these decompositions may also be produced by heat; but this is not always the case.

Repeated discharges from the common electrical battery decompose oxide of mercury into mercury and oxygen gas. Bonnijol decomposed chloride of silver, and even hydrate of potash enclosed in glass tubes, by repeated electric sparks; the silver separated in ten minutes; the potassium burnt immediately after separation.

Continued discharges from the common battery, or even simple electric sparks, partially decompose carbonic acid gas into oxygen and carbonic oxide, olefiant gas and light carburetted hydrogen into carbon and hydrogen gas,—likewise phosphuretted hydrogen, sulphuretted hydrogen, hydriodic acid, hydrochloric acid, and ammoniacal gases, into phosphorus, sulphur, iodine, chlorine, and nitrogen, on the one hand, and hydrogen on the other.

B. Decompositions produced by the continuous Discharge of Electricity of small Tension.

If the two electricities proceeding from the poles of a voltaic battery, or any other suitable source, be made to flow through two good conductors, not in contact with each other, into a compound liquid, the three *following cases* may arise.

1. The liquid conducts the electric current very well, and gives passage to it, without undergoing any alteration.—This is the case with solutions of various metals in mercury, and with fused alloys.

2. It completely stops the current, and suffers no decomposition: if, however, the electricity possesses great intensity, it may force a passage mechanically through the liquid.

3. The liquid allows more or less readily the continual ingress of the two electricities, but is at the same time decomposed; and only in so far as the decomposition goes on, is the passage of the current possible,—so that the (apparent) conducting power of the liquid is directly proportional to its decomposibility, or else identical with it.—To this class belong all liquids mentioned on page 311, under the head *b*, with the exception of fused protiodide of mercury, which conducts well without being decomposed.

All gases act as non-conductors, and are not decomposible by electricity of small tension. Solid compounds likewise resist decomposition, in consequence of the immobility of their particles, excepting when they are in contact with liquids on which the electric current acts.

In the decomposition of liquids of class 3, the elements are always liberated close to the conductors by which the two electricities are introduced,—and, according to their different natures, are either evolved in gas-bubbles or deposited in the solid form, or dissolve in the undecomposed portion of the liquid surrounding the conductor, or combine chemically either with the conductor or with other elements of the liquid, thereby giving rise to *Secondary Products*.

The two good conductors by which the two electricities are introduced into the liquid are the *Polar Conductors*, *Polar Wires* (they may, however, consist of charcoal, graphite, or mercury), or Faraday's *Electrodes*.—The conductor which introduces the positive electricity is the *Positive Polar Wire*, Faraday's *Anode*, Smee's *Oxode*, Graham's *Zincode* or *Zincoid*.—The conductor which introduces the negative electricity is the *Negative Polar Conductor*, Faraday's *Cathode*, Smee's *Hydrogode*, Graham's *Platinode* or *Chloroid*.—The liquid decomposed by the electric current is Faraday's *Electrolyte*, and the decomposition produced by electricity, *Electrolysis*.—The elements of the liquid evolved on the polar conductors are Faraday's *Ions;* the electro-negative elements evolved at the positive conductor or anode being called *Anions*, and the electro-positive elements evolved at the negative conductor or cathode, *Cations*. —The vessel in which the decomposition of the liquid takes place is called the *Decomposing Cell*.

[Electrolytes must be regarded as non-conductors, which, though they may be broken through by electricity of high tension, will not allow electricity of low tension to pass quietly through them. In the latter case, therefore, the two electricities are unable to combine with one another; but they may unite with the elements of the liquid. It has been assumed (pp. 157 and 342) that hydrogen, when in the free state, contains negative electricity, and oxygen positive electricity combined with it,—and that when these two bodies unite, the two electricities combine together and form heat, which is partly set free, and partly perhaps remains combined with the water. Now when negative electricity acts on one part of the water, and positive electricity on another, the former unites with the hydrogen of the contiguous atom of water, the latter with the oxygen of another atom of water: hence hydrogen gas is evolved at the cathode,

and oxygen at the anode. The electric fluids entering the liquid with a certain tension, and in a certain quantity, their affinity for oxygen and hydrogen overcomes the mutual attraction between those elements, somewhat in the same manner as the increased affinity of caloric for carbonic acid at a red heat decomposes carbonate of lime. Moreover, while an atom of hydrogen is evolved at the negative conductor, and an atom of oxygen at the positive, a transposition of atoms (as described at p. 343, *f*) takes place throughout the row of atoms of water lying between these points; so that the liquid in the middle remains quiet, and no transference of matter from one electrode to the other can be detected. The greater, however, the distance between the points at which the electrodes dip into the liquid, and the greater, therefore, the number of atoms which must be transposed, the higher will be the electrical tension required to overcome this resistance.

As with water, so also with all other electrolytes;—their cation, a metal for example, resumes the negative electricity which it had lost on combining with the anion, such as chlorine, bromine, iodine, &c.,—and this again resumes its positive electricity. In all these cases, the negative electricity which the cation takes up must correspond to the positive electricity taken up by the anion,—that is to say, the required quantities of electricity must be to one another in the proportion in which they combine to form heat.

When the oxygen liberated at the anode is not evolved as gas but combines with the anode—*e. g.*, when the latter consists of zinc—we may suppose that the negative electricity, as it is set free, combines with the positive electricity proceeding from the battery, and that in this case the decomposition is effected by the affinity of negative electricity for hydrogen and of zinc for oxygen.

According to this view, electrolytes are not really conductors,—they do not permit the combination of the two electricities,—no electric current passes through them,—but their elements continually take up the elective fluids as they enter, and thus give rise to a constant current in the electrodes. The apparent conducting power of electrolytes is greater therefore in proportion to the facility with which they are decomposed, that is, to the rapidity with which their elements take up the electric fluids proceeding from the battery, and separate from the liquid.

We are at present unable to explain why pure water resists the transposition of its atoms with greater force than water combined with acids or salts.]

[The theory here given of decomposition by the electric current is in the main the same as that of Grotthuss. (*Ann. Chim.* 58, 65; 63, 34.) That philosopher likewise supposed that, in the decomposition of water, positive electricity combines with the oxygen of the atom of water lying next to the positive wire, and negative electricity with the hydrogen of the atom of water next to the negative wire, and that between the two poles transposition of atoms takes place. The production of flame, which accompanies the combination of oxygen and hydrogen gas, was likewise attributed by Grotthuss to the combination of the positive electricity in the oxygen with the negative electricity in the hydrogen. The only difference between his theory and the preceding is that he supposes a linear transposition of atoms to take place (something like that represented in *App.* 23, instead of a semicircular up and down motion. Sir H. Davy (*Gilb.* 28, 39) and W. Henry (*Ann. Phil.* 1, 465) propounded

views similar to that of Grotthuss. Becquerel (*Ann. Chim. Phys.*) supposes, as I do, that the atoms move in semicircles one over the other. According to Faraday (*Phil. Trans.* 1833, II., 675; also *Pogg.* 32, 401), who admits but one kind of electricity, electrolytic decomposition is the result of a peculiar corpuscular action developed in the direction of the current; it proceeds from a force which is either added to the affinity of the bodies present or determines the direction of that force. The decomposing body is a mass of acting particles, of which all that lie in the course of the current contribute to the terminal action; and in consequence of the affinity between the elements being weakened or partially neutralized by the current, parallel to its own course in one direction, and strengthened and assisted in the other, the combined particles acquire a tendency to move in different directions. The particles of one element *a* cannot travel from one pole to the other, unless they meet with particles of an opposed substance *b* ready to move in the opposite direction. For, in consequence of their increased affinity for these particles, and the diminution of their affinity for those which they have left behind them in their way, they are continually driven forward. Faraday, therefore, likewise supposes a transposition of particles. According to De la Rive (*Ann. Chim. Phys.* 28, 190), the positive electricity which enters a liquid—water for example—combines with the hydrogen, setting the oxygen free, and carries the hydrogen rapidly along with it through the whole mass of liquid till it reaches the negative wire; it then enters the wire, while the hydrogen combined with it escapes in the form of gas. At the same time, the negative electricity proceeding from the negative wire liberates hydrogen from the contiguous atom of water, carries the oxygen of the same atom over to the positive wire, enters the wire, and sets the oxygen free. Hence the oxygen gas evolved at the positive pole proceeds from two sources—half from the positive, and half from the negative current; similarly with respect to the hydrogen gas.—This view is mainly liable to the objection, that when the polar wires dip into two different liquids, the anions of the liquid which is in contact with the negative wire usually require a long continued action of the current to bring them to the positive pole, and sometimes do not reach it at all;—similarly, with regard to the passage of the cations of the other liquids towards the negative pole. For example, when solution of sulphate of magnesia is placed in contact with the positive pole and water in contact with the negative pole, no magnesia is set free at the latter, the whole of that substance being precipitated at the surface of separation of the two liquids. According to Biot, a liquid placed in the voltaic circuit divides itself into two halves, one of which acquires a positive the other a negative electrical tension. Each element of the liquid then goes towards that side which is charged with the kind of electricity opposite to its own, and thus decomposition ensues. But the evolution or precipitation of the elements does not take place throughout the two halves of the liquid—but, for the most part, solely at the polar wires.]

Electrolytes, Ions, and Products of Decomposition in general.

According to Faraday, only those compounds of the first order are directly decomposible, which contain one atom of one of their elements for each atom of the other,—*e. g.*, compounds of 1 At. hydrogen or metal with 1 At. of oxygen, iodine, bromine, chlorine, fluorine, or cyanogen, &c. On the other hand, boracic acid (BO^3), sulphurous acid (SO^2), sul-

phuric acid ($S O^3$), iodide of sulphur, chloride of phosphorus ($P Cl^3$) and ($P Cl^5$), chloride of sulphur ($S^2 Cl$), chloride of carbon ($C^4 Cl^6$), bichloride of tin ($Sn Cl^2$), terchloride of arsenic ($As Cl^3$), quintochloride of antimony ($Sb Cl^5$), and acetic acid in the liquid but anhydrous state, are undecomposible and act as non-conductors. Oxide of antimony and terchloride of antimony, which are decomposible in the fused state (the latter however but slightly), form an exception not yet explained; so likewise does protiode of mercury ($Hg I$), which in the melted state conducts without suffering decomposition.—All compounds which are decomposible when dissolved in water, behave in the same manner when fused. (Faraday.)

Connell found that when the electric current was conducted into fused iodic acid ($I O^5$), the galvanometer was deflected and the acid decomposed: he considers however that the decomposition may be the result of heat, inasmuch as the fusing and decomposing points of the acid are near to one another. Liquid ammonia—possibly from containing a trace of water—conducts slightly the electricity of a battery of 250 pairs, so that an agitation is perceptible in it; but water placed in the same circuit is not decomposed. (Kemp.)—Liquid cyanogen does not conduct the electricity of a battery of 300 pairs of plates. (Kemp.)

Of the elements (and substances like ammonium and cyanogen, which replace them in their combinations), some are always evolved at the negative, others always at the positive pole, with whatever other substance they may be combined:—hence they are divided into cations, which are evolved at the negative electrode, and anions which are evolved at the positive electrode.—The *Anions* are: Oxygen, fluorine, chlorine, bromine, iodine, and cyanogen,—probably also sulphur, seleninm and sulpho-cyanogen (For the acids also included in this class by Faraday, *vid. Decomposition of Salts*).—The *Cations* are: Hydrogen, the alkali-metals, magnesium, manganese, antimony, bismuth (?), zinc, cadmium, tin, lead, iron, cobalt, nickel, copper, mercury, silver, gold, platinum (and ammonium). The salifiable bases are also classed by Faraday under this head (*vid. Decomposition of Salts*).—All the elements are probably ions; but with respect to some among them, nothing has yet been determined by experiment. (Faraday.)

It is necessary to distinguish, as Faraday does, between *direct* and *indirect* decomposition by the electric current. The former arises from the immediate action of the current; but the substances thereby liberated at the electrodes, may, when the liquid is a mixture of several compounds, exert a decomposing action on a compound upon which the current does not act directly. Thus, aqueous ammonia is resolved by the electric current into hydrogen gas at the negative and nitrogen gas at the positive pole. It may be supposed that the water alone is directly decomposed; and that the oxygen separated at the positive pole, abstracts hydrogen from the ammonia and sets free the nitrogen of the same compound. It cannot however be positively determined, either in this or in many other cases, which decomposition is direct and which indirect.

Degree of Decomposition.

When the electric current continues for a sufficient length of time, the decomposition is complete. If the two electricities be conducted into two cups containing dilute solution of sulphate of potash, and connected by a moistened wick of asbestus, which is washed twice a day, so that no salt may be deposited upon it,—the positive cup is found, after three

days, to contain all the sulphuric acid, and the negative cup all the potash. (H. Davy.)

Place of Decomposition.

The separation of the ions takes place only in the immediate neighbourhood of the electrodes, not at any part of the liquid at a distance from them. (H. Davy, De la Rive.) If a solution of common salt, coloured with infusion of violets, be divided into three portions by two membranous partitions—the electrodes dipping into the outermost divisions—the colour of the liquid changes in these divisions alone, not in the middle. (De la Rive.)

When a number of currents, either equally or unequally strong, pass simultaneously through the same liquid, either in the same or in opposite directions, neither of them is disturbed by the rest. (Marianini.)

Relation between the Quantity of the Electric Current and the Quantity of Liquid decomposed.

A battery which retains a platinum wire $\frac{1}{101}$ of an inch thick in a state of constant ignition during the whole time occupied by the decomposition, decomposes one grain of water in $3\frac{3}{4}$ minutes: this quantity of electricity is perhaps equal to that of a powerful stroke of lightning. (Faraday.)

The quantity of electricity which enters the liquid is directly proportional to the quantity of liquid decomposed. Hence, the quantity of electricity in the current may be determined from the quantity of the products of decomposition. (Faraday, De la Rive.) The greater therefore the quantity of electricity which the apparatus employed yields in a given time, the greater will be the quantity of liquid decomposed, provided that the electricity possesses the requisite tension. Hence the batteries of Grove, Daniell, Sturgeon, Smee, and others, have the strongest decomposing action, the electrical machine the weakest.

Faraday's *Volta-electrometer* or *Voltameter*. Into the lower part of a graduated tube closed at the top (*App.* 28) are inserted, opposite to each other, two platinum wires, to the ends of which are attached two small plates of platinum placed upright in the tube. The open end of the tube is inserted into one aperture of a vessel, two-thirds filled with dilute sulphuric acid of sp. gr. from 1·25 to 1·336, the other aperture being closed with a stopper. The tube is filled with liquid by inverting the apparatus. It is then placed upright, and the two platinum wires connected with the poles of the battery, in order to determine the quantity of detonating gas evolved in a given time. The decomposition must not be allowed to go on long enough to bring the gas in contact with the platinum plates, because these plates would give rise to a slow re-union of the gases.—In many liquids, as in hydrochloric acid, only hydrogen gas has to be collected, in others only oxygen, as in the case of sulphate of copper. In such cases, the voltameter may be formed of a graduated tube, having a platinum wire inserted into its upper and closed end, filled with the liquid, and inverted in a glass vessel into which the other electrode is introduced (*App.* 29). Other arrangements are likewise described by Faraday.

Whether the quantity of electricity in the current be measured by the voltameter or by the galvanometer (in proportion to the tangent of the

deflection, and therefore by means of Nervander's compass) or by the electro-magnetic balance, the proportion obtained is invariably the same. (Jacobi.)

An atom of any one electrolyte requires for its decomposition the same quantity of electricity as an atom of any other, whether the combination be held together by strong or by feeble affinity.

If the current of a battery be passed through the voltameter, and thence —by means of a platinum wire entering at the upper end and conveying positive electricity—into a glass tube containing fused protochloride of tin, and having inserted into its lower end, a platinum wire, which serves as the negative electrode,—then, for every 9 parts of water decomposed in the voltameter, 58·53 parts of tin are deposited on the last-mentioned wire (the atomic weight of tin is 59).—When fused chloride, iodide, oxide, and borate of lead, were treated in a similar manner, the quantity of lead obtained was too small in proportion to the water decomposed, viz.: to 9 parts of water, 100·8, 89, 93·2 and 101·3 lead, whereas the atomic weight of lead is 103·8. The cause of the deficiency is probably that a portion of the precipitated lead was redissolved by the anion. When two silver wires are introduced as electrodes into fused chloride of silver, the weight of the positive electrode diminishes almost exactly by 108·1 parts of silver for every 9 parts of water decomposed in the voltameter, whilst that of the negative electrode increases by the same quantity. Chloride and iodide of lead treated in the same manner, lead being used as the positive electrode, give 101·5 and 103·5 lead for every 9 parts of water. (Faraday.)

If the same current be made to pass through fused chloride of lead and solution of Glauber's salts, one atom of Glauber's salt is decomposed for every atom of lead reduced. If instead of Glauber's salt a solution of common salt be used, the electricity being conducted into it by means of a weighed tin plate, then for every atom of lead reduced, one atom of soda is separated, and one atom of tin dissolved. (Daniell.)

If the current of a battery be passed through a number of metallic solutions connected by platinum wires, the metals are precipitated in the ratio of their atomic weights,—*e. g.*, about four times as much silver as copper. (Matteucci.)

For Berzelius's objections to Faraday's law—that equal numbers of atoms of liquid require equal quantities of electricity to decompose them—vid. *Berzelius' Jahresb.*, 15, 34.

The quantity of electricity which an atom of liquid requires to decompose it, is equal to the quantity which an atom of the same liquid evolves during its electro-chemical decomposition by ponderable bodies. (Faraday.)

If an atom of hydrogen has given up a quantity of negative electricity, denoted by x, and an atom of oxygen the same quantity of positive electricity, in combining to form water, this same quantity of electricity must be restored to each of them by the current.—When an atom of water is decomposed by an atom of zinc which combines with its oxygen, x units of negative electricity are set free from the zinc,—while the atom of hydrogen evolved on the copper, takes x units of negative electricity from it, and sets free x units of positive electricity, which flow through the connecting wire to the x units of negative electricity liberated from the zinc].

The following experiments afford an approximate demonstration of this law; but the quantity dissolved in each cell of the battery in proportion to 9 parts (1 At.) of water in the voltameter, was always greater than

32·2 parts (1 At.), on account of pure chemical action, which could not be altogether prevented.

When a Daniell's constant battery, with amalgamated zinc was used, 33·6 parts of zinc were dissolved in each cell of the battery for every 9 parts of water decomposed. (Jacobi.)

With batteries containing only one liquid, the loss of zinc is greater. When the form of the battery and the nature of the liquid are varied, the following differences are observed,—F. denoting Faraday's apparatus, with double copper surface (p. 424); Tg. the common trough-battery, with single copper surface; Q Z. the surface of the plates in square inches, P Z. the number of pairs; 1 Tr. the number of atoms of zinc dissolved in one trough during the decomposition of one atom of water; and Tot. the number of atoms of zinc dissolved in all the troughs taken together. In both batteries, the liquid used was a mixture of 200 measures of water, 4·5 of oil of vitriol, and 4 of strong nitric acid.

	Q Z.	P Z.	1 Tr.	Tot.	Q Z.	P Z.	1 Tr.	Tot.	Q Z.	P Z.	1 Tr.	Tot.
F...	3	40	2·25	88·4	4	20	3·7	74	4	10	6·76	67·6
Tg..	4	40	3·54	141·6	4	20	5·5	110	4	10	15·5	155·0

When different liquids are used in a Faraday's battery of forty pairs, the quantities of zinc dissolved in each cell for one atom of water decomposed are as follows: With 200 measures of water mixed with 8 of strong nitric acid, 1·85 At.; the same quantity of water with 16 nitric acid, 1·82; with 32 nitric acid, 2·1 At.; with 16 measures of strong hydrochloric acid, 3·8; with 9 measures of oil of vitriol, 4·66; with 16 measures of strong hydrochloric and 6 of nitric acid, 2·11; with 4·5 measures of oil of vitriol and 4 of nitric acid, 2·26; with 9 measures of oil of vitriol and 4 of nitric acid, 2·79; and with 9 measures of oil of vitriol and 8 of nitric acid, 2·26 At. zinc. Nitric acid is therefore the best for this battery; and different degrees of dilution of this acid do not affect, to any considerable extent, the proportion between water decomposed and zinc dissolved. (Faraday.)

If the current from about four pairs of zinc and copper be made to pass into a solution of nitrate of silver, and the quantity of zinc dissolved be the same one time as another, the quantity of silver separated will likewise be constant,—whether the zinc be quickly dissolved by the use of strong and warm acid, and the galvanometer strongly deflected by the current—or the zinc be slowly dissolved by cold, weak acid, and the galvanometer feebly deflected. The same quantity of electricity passes through the liquid in both cases, though in different times: hence the quantity of silver precipitated is likewise the same. Similar results are obtained with a battery of copper, platinum, and nitric acid.—If a pile *a* be constructed of lead and platinum plates, and a pile *b* of copper and platinum, the weight of the lead plates being to that of the copper plates in the ratio of the atomic weights of the metals, viz., as 103·8 : 32,—and the currents of both batteries be passed through solution of nitrate of silver contained in separate vessels,—then, when all the copper and lead are dissolved, the quantities of silver separated in the two vessels will be found to be equal. (Matteucci.)

Since an *electrical machine* developes much less electricity in a given time than a galvanic battery, even with very small plates, it does not readily produce decomposition, notwithstanding its high tension. When the machine is employed for this purpose, the two electrodes are connected with the two coatings of the electrical battery, or one with the conductors and the other with the rubber or the ground. The excessive tension of

the electricity must be weakened by giving a large surface to the battery or the conductor, or else by passing the charge through a wet string, so that it shall no longer burst violently through the electrolyte; and its deficiency in quantity must be compensated by properly enveloping the electrode, so as to concentrate the electricity at its entrance into the liquid upon a small point.

Wollaston fused fine gold or silver wires into glass or sealing-wax, so that only the extreme points of the wires came in contact with the liquid. In this manner he decomposed water, and sulphate of copper and corrosive sublimate dissolved in water, by about 100 turns of the machine. But in this decomposition of water, both oxygen and hydrogen were evolved at each electrode—a result probably arising from the great intensity of the electricity, which Wollaston took no means to counteract.—Sir H. Davy effected in two hours, by Wollaston's method, the decomposition of aqueous solution of sulphate of potash contained in two cups connected by asbestus. (*Comp.* Gahn. and Hisinger, *Gilb.* 27, 311.)—Bonnijol (*Bibl. univ.* 45, 213) decomposed water by friction electricity, and likewise by atmospheric electricity, which he caused to enter the liquid by wires half a millimetre in diameter.

When only one wire is surrounded with sealing-wax, detonating gas is evolved only on this one in pure water; none on the other. The stronger the sparks, the greater is the quantity of detonating gas evolved; and when the sparks cease, the gas produced is diminished to a mere trace. A solution of sulphate of soda yields but a trace of gas, even when strong sparks are passed. Hence the decomposition of water by machine electricity is different from that produced by galvanic electricity. (Faraday.)

When moistened litmus paper is connected with the wire of the conductor of the electrical machine, and moistened turmeric paper with the wire of the rubber, and the two papers united by means of a thread seventy feet long moistened with solution of turmeric paper,—decomposition takes place (and therefore reddening of the litmus paper by evolved acid and browning of the turmeric paper by liberated alkali) as strongly as when the two papers are united by a shorter connection. This is due to the high tension of the machine electricity. Similar remarks apply to the decomposition of iodide of potassium. (Faraday.)

It is not even necessary to have the circuit regularly closed. If moistened litmus paper be connected with the conductor (or turmeric paper with the rubber) and likewise with a string saturated with sulphate of soda, and communicating with the ground (or the gas-pipes of London), or even if the paper connected with the conductor or the rubber be insulated,—decomposition ensues, in consequence of the combination of the highly intense electricity of the machine with the opposite electricity proceeding from the latent electric fluid of the earth or the air. Hence the opposite reaction shows itself at the part of the paper farthest from the point at which the electricity of the machine enters. If a thread, wetted with solution of sulphate of soda and attached to the conductor, be brought in contact with turmeric paper connected by a wire with the gas-pipes under ground, the paper becomes reddened by the negative electricity which flows from the earth into the liquid. A similar effect is produced upon litmus paper connected in like manner with the rubber. If a piece of litmus paper and a piece of turmeric paper in the form of acute triangles, be moistened with solution of sulphate of soda, laid together by their shortest sides, and placed between conducting wires attached to the conductor and rubber of the machine—the ends of the wires being about half

an inch distant from the points of the papers—reddening takes place at both points, but disappears again when the points are turned round, so as to bring the turmeric paper opposite to the positive conductor. The two paper triangles may also be laid upon glass, and connected with the two conductors by strings, six inches long, moistened with solution of sulphate of soda.—Solutions of iodide of potassium and acetate of lead give corresponding results. (Faraday.)

If the electricity from the machine be communicated through the medium of a wet string or a wire, or in small sparks, to an electrode dipping into a liquid,—a solution of iodide of potassium mixed with starch is turned blue by half a turn of the machine—solution of sulphate of soda reddens litmus and turmeric paper after two or three turns—hydrochloric acid evolves chlorine—and sulphate of copper deposits copper on the silver cathode after twenty turns. (Faraday.)

Aqueous solution of iodide of potassium, contained in a small U-tube, into which are immersed platinum wires proceeding from the conductor and the rubber, acquires a yellow colour in the positive arm. (Henrici, *Pogg.* 47, 431.)

Influence of the Intensity of the Current on Decomposition.

[The more readily the atoms of a liquid are transposed—whether from its peculiar nature or from the thinness of the film of liquid between the electrodes,—the smaller is the tension which the electric current requires in order to penetrate it, the greater the quantity of electricity which flows into the liquid from a given source, and the greater the quantity of liquid decomposed in a given time. If, however, by increasing the number of pairs, or otherwise, the tension has been raised to such a degree, that all the electricity evolved from the source in a given time is able to enter the liquid—so that the galvanometer shows the same deflection whether the circuit be closed by a metallic conductor or by a liquid—a further rise of intensity does not accelerate the decomposition.]

Aqueous solution of iodide of potassium may be decomposed by a current of the smallest tension; next in order of facility come fused chloride of silver, fused protochloride of tin, fused chloride of lead, fused iodide of lead, water containing hydrochloric acid, water containing sulphuric acid. That the chloride of lead is more easily decomposed than the iodide, perhaps arises from the platinum electrode having a greater affinity for chlorine than for iodine. (Faraday.)

If the cells *a* and *b* (*App.* 30) contain dilute sulphuric acid of 1·25 sp. gr.,—*o*, *p*, and *i* being platinum, *g* amalgamated zinc, and *h* a platinum plate, on which is laid a piece of paper moistened with solution of iodide of potassium, and having the end of the platinum wire placed in contact with it,—continued decomposition of the iodide of potassium takes place, whilst on the two platinum plates immersed in *b* not a single gas-bubble appears, even in the course of several days. Even when the paper at *h* is removed and metallic contact established, not a particle of gas is evolved in *b*; neither does any evolution of gas ensue, when the cell *b* contains aqueous solution of potash instead of sulphuric acid. But when to the sulphuric acid in *a* a little nitric acid is added, an evolution of gas takes place on the platinum plates in the course of twelve seconds, because the nitric acid increases the intensity of the electric current. (Faraday.)

If two pieces of paper lying on platinum plates are placed in the current of a single pair of amalgamated zinc and platinum immersed in

solution of common salt,—one of the papers being moistened with solution of iodide of potassium, the other with solution of sulphate of soda, and the latter placed between moistened litmus and turmeric papers,—and the circuit is closed by a bent platinum wire, whose ends rest on the two papers, the iodide of potassium is decomposed, but not the sulphate of soda, not even when the iodide of potassium paper is removed, and metallic contact established. If one of the platinum plates be replaced by a capsule, in which nitre or chloride of lead is maintained in a state of fusion—the zinc and platinum plates being immersed in dilute sulphuric acid—the iodide of potassium is decomposed, but not the nitre or the chloride of lead: chloride of silver, on the contrary, is decomposed as readily as the iodide of potassium. It appears then that water, solution of sulphate of soda, chloride of lead, and iodide of lead, can give passage to currents of very small intensity without being decomposed. (Faraday.)

The current from a single pair does not decompose water, and yet produces deflection of the galvanometer. If the current of a ten-pair battery be weakened by the interposition of a long thin wire, to such a degree that it produces the same deflection as the current of a single pair, it will behave towards water in the same manner as the latter. Hence feeble currents pass through water without decomposing it. (Jacobi.)

It is true that no gas is obtained when a feeble current is conducted into a watery liquid by means of platinum plates: nevertheless, the water is decomposed—but so slowly, that the oxygen and hydrogen gases liberated on so large a surface partly surround it as an envelope, and are partly absorbed by the water. Even when two fine platinum wires are used as electrodes, not a single bubble of gas escapes. But if one electrode consists of a platinum plate, the other of a fine wire of the same metal covered with glass up to its point, according to Wollaston's method (p. 438), gas is evolved at the point of the wire—though only for a short time—when the water is subjected to the action of a pair of plates of zinc and platinum in solution of common salt. The evolution of gas is renewed, both when the surface of the larger electrode is increased, and likewise when the current is reversed. The gas appears at the narrow electrode, because the wider surface of the other greatly facilitates absorption. When the electrodes have equal surfaces, the positive electrode becomes negative, in consequence of a film of oxygen attached to it—and the negative electrode positive, from a film of hydrogen; and thus the primitive current is weakened (*vid. Secondary Currents*), so that the water is decomposed at the same rate only as absorption goes on.—Sulphate of soda may also be decomposed by the current of a pair of zinc and platinum in solution of common salt, by means of electrodes of very unequal surface like those above described. (Andrews, *Pogg.* 41, 166.)—Grove also (*Pogg.* 48, 305) concludes from his experiments, that water does not conduct the electric current without undergoing decomposition.

The current from a single pair of amalgamated zinc and platinum plates in dilute sulphuric acid, however strong, though it always decomposes iodide of potassium, does not [visibly] decompose acidulated water or solution of nitrate of silver. The two last mentioned liquids are not decomposed even when the plates are immersed in dilute sulphuric acid; but when a small quantity of nitric acid is added to the liquid in the exciting cell, decomposition takes place. But the current of a pair of zinc and copper, having the surface of a square metre and immersed in dilute sulphuric acid, without any nitric acid, likewise decomposes nitrate of silver,—because this large pair develops a greater quantity of electri-

city. Hence decomposition depends only on the quantity of electricity. (Matteucci.) [That however the intensity of the current exerts great influence, is evident from the fact that combination of a number of pairs of plates however small will decompose any electrolyte whatever.]

If the electrodes, dipping into acidulated water, consist of one of the more oxidable metals instead of platinum [in which case the affinity of those metals for oxygen will favour the decomposition] then, according to Henrici, the current of a single pair consisting of zinc, dilute sulphuric acid, sulphate of copper, and copper, will decompose water and evolve hydrogen gas, the deflection of the galvanometer increasing as follows, with the quantity of gas obtained in an hour:

	Platinum.	Silver.	Copper.	Brass.	Steel.	Tin.	Zinc.
Cub. centim. Hydrogen gas	0	0·3	12	19	34	36	72
Sine of angle of deflection	0° 1′	0° 6′	0° 8′	0° 18′	8° 26′	9° 11′	28° 17′

Some decomposition of water is doubtless effected with platinum electrodes, but as the oxygen evolved does not combine with the platinum the action is retarded. (Henrici.)

To this head likewise belong the experiments mentioned, pp. 403....408.

Thermo-electric currents, weak both in quantity and intensity, decompose nitrate of silver, when the electrodes consist of platinum,—but not salts of copper, lead, tin, or zinc; in these also electrodes of gold or silver produce no effect. But when the electrodes consist of the same metal as that in the solution, decomposition is easily effected—*e. g.* nitrate of silver with silver electrodes, sulphate of copper with copper, protochloride of tin with tin, acetate of lead with leaden electrodes. Platinum wires in solutions of platinum produce no effect. A thermo-electric current is best conducted into a solution of common salt by means of wires of zinc, tin, lead, or iron,—less readily by copper, with difficulty by silver, and not at all by platinum. Similar to the action of the thermo-electric current is that of the very feeble current obained when the vessel *a* (*App.* 2) contains potash, *b* nitric acid, and the asbestus fibres *h* solution of common salt—platinum wires dipping into *a* and *b*, and being connected with wires of the metals above mentioned. (Becquerel.) [In this case, the electricity has no affinity to overcome—because, for every portion of metal separated at the cathode, an equal portion combines with oxygen and acid at the anode, so that the electricity has only to transpose the atoms.]

The following experiments were made to determine the proportion in which the decomposition of different liquids,—and therefore also the quantity of the current, increases with the number of pairs:

In A a pile was constructed of zinc and copper with solution of sal-ammoniac, in B with water containing nitro-sulphuric acid, and in C with spring-water; in D a battery of zinc and platinum in dilute sulphuric acid was employed.—The liquid in the decomposing cell was water = Aq, or a solution of 1, 4, 8, or 10 parts of sal-ammoniac in 100 parts of water = Sm 1, Sm 4, Sm 8, Sm 10; or saturated solution of sal-ammoniac = Sm g; or dilute sulphuric acid = S f; or a solution of 1 part of sulphate of zinc (zinc-vitriol) in 100 parts of water = Z V; or solution of iodide of potassium = I K.—P Z denotes the number of pairs employed.—The degrees under A, B, C give the deflection of the galvanometer; the numbers under D denote the relative quantity of hydrogen gas evolved from the solution of iodide of potassium. (Matteucci.)

	A.					B.			
P Z.	Aq.	Sm 1.	Sm 4.	Sm 10.	Sf.	Aq.	Sm 1.	Sm 8.	Sm g.
8	½°	5°	8°	9°	10°	1°	7°	15°	38°
16	½	12	17	21	27	2	14	34	60
24	1	15	19	26	27	3	22	40	
32	3	16	22	27	27	6	25	60	
40	3	18	27	27	27	6	33	74	

	C.				D.	
P Z.	Aq.	Sm g.	Z V,	P Z.	I K,
10	1½	14°	2°	1	1
20	1½	17	3	2	8
30	2	18	7	3	17·5
40	2	15	8	4	65
50	3	12	7		
60	3	11	7		

In the following experiments of Jacobi and Walker, Daniell's constant battery was used. The quantity of detonating gas developed in the decomposing cell in a given time, according as a greater or less number of plates were connected together, was determined in measures. In Jacobi's experiments and in those of Walker, given under *a* and *b*, the decomposing cell contained water acidulated with sulphuric acid; in *c* it contained distilled water.

Jacobi.				Walker.			
P Z.		P Z.		P Z.	*a*.	*b*.	*c*.
2	1	8	54	20	1	– 1	–
3	12	9	59	40	1·2	– 1·06	– 1
4	22	10	67	60	1·3	– 1·06	– 1·57
5	33	11	68	80	1·4	– 1·12	– 2·13
6	42	12	75	100	1·5	– 1·12	– 3·47
7	49	13	80	120	1·55	– 1·12	– 3·88
				140	1·5	– 1·16	– 6·60
				160	1·5	– 1·19	– 8·25

Influence of the Chemical Nature of the Electrolyte on its Decomposition.

The [apparent] conducting power of liquids for electricity—*i. e.* their susceptibility of decomposition by the electric current—is usually determined by placing them, together with a galvanometer, in an electric current of constant tension, and determining by how much the quantity of the current (the deflection of the galvanometer) is diminished by the interposition of the liquid. The wires or plates immersed in the liquid must be at the same distance from one another in all cases. The differences of conducting power appear to be so much the greater, as the tension of the current is less, and become less perceptible as the tension increases.

The small conducting power of pure water is considerably increased by the solution of other substances in it (p. 311, *b*).

The (very weak) thermo-electric current of a single pair of bismuth and antimony is very easily conducted by the aqueous solution of yellow sulphuret of potassium, by a mixture of hyponitric acid with an equal quantity of water, by red fuming nitric acid, and by a mixture of one measure of oil of vitriol with two measures of strong solution of sulphate of copper; it is also conducted tolerably well by yellow nitric acid, and by a mixture of two measures of oil of vitriol and one measure of water;—slightly by nitric acid freed by boiling from hyponitric acid, and by oil

of vitriol;—very slightly by solution of potash, and not at all by anhydrous hyponitric acid. (Faraday.)

The conducting power of platinum is 2546680 times greater than that of a saturated solution of sulphate of copper. Assuming the latter = 1, that of a mixture of 1 measure of solution with 1 measure of water = 0·64, with 2 measures of water = 0·44, with 4 measures of water = 0·31; that of a saturated solution of sulphate of zinc = 0·417; that of a mixture of water with $\frac{1}{20000}$ nitric acid = 0·015; and that of pure water 0·0025. (Pouillet.)

The current of a 40-pair battery passed through pure water gives only $\frac{1}{15}$ as much detonating gas in a given time, as when the decomposing cell contains dilute sulphuric acid. (Faraday.)—Water becomes much more easily decomposible when mixed with sulphuric acid than when saturated with common salt. (Henrici.)

The current of a pair of zinc and copper plates in saturated solution of common salt, conducted by means of two gilt brass plates into the undermentioned liquids (all the solutions are saturated) produces the following deflections of an interposed galvanometer: Pure water, $\frac{1}{2}°$; acetate of lead, 3...4°; sulphate of potash or soda, nitre, chloride of calcium, or chloride of lead, 5°; chlorate of potash, 7°; borax, chloride of manganese, tartrate of potash, tartar emetic, acetate of soda, or benzoate of potash, 10°; carbonate of potash or soda, 11°; green vitriol, nitrate of lead, or acetate of potash, 12°; oxalate of potash, 13°; aqueous ammonia of sp. gr. 0·980, or tartaric acid, 15°; protochloride of tin, 10...20°; alum or sulphate of copper, 20°; sulphate of zinc, 22°; dilute phosphoric acid, 23°; strong vinegar, 25°; mixture of 1 part oil of vitriol and 4 parts water, 28°; nitrate of mercury, 30°; English oil of vitriol, 30...32°; nitrate of silver (solution not quite saturated), 35°; dilute nitric acid, sal-ammoniac, or sesqui-chloride of iron, 42°; bichloride of platinum, 45°; dilute hydrochloric acid, 50°.—When a large pair of zinc and copper plates is excited by solution of common salt, the deflections are stronger, but the differences with respect to the various liquids smaller. (Pfaff, *Schw.* 55, 258.)

The current of the same battery passed through various acids of different degrees of concentration, produces, according to Matteucci, the following deflections:

	Sp. Gr.	Galv.	Sp. Gr.	Galv.	Sp. Gr.	Galv.
Sulphuric acid	1·850	35°	1·022	36°	1·010	36°
Nitric acid.....	1·180	57	1·029	47	1·015	37
Hydrochloric acid* ..	1·260	58	1·027	50	1·015	57

If the deflection produced by 1 part of sal-ammoniac in 100 parts of water amounts to 12°, it will be 22° with 2 parts of sal-ammoniac, 26° with 3 parts, and 27° with 4 parts.—If 1 part of sulphate of zinc in 100 of water gives 3° deflection, 2 parts of the same salt will give, 5°,—3 parts, 6·5°,—4 parts, 8°,—5 parts, 13°,—6 parts, 17°,—7 parts, 23°,—and 8 parts, 24°. If a solution of 1 part of sal-ammoniac in 100 water gives a deflection of 12°, and a solution of 1 part of nitre in 100 water, a deflection of 8°, a solution of sal-ammoniac and 1 nitre in 100 water, will produce a deflection of 12° + 8° = 20°. The same simple addition takes place with other aqueous and alcoholic solutions. Hence, when 1 part of sal-

* Since hydrochloric acid never has the sp. gr. 1·26, it is probable that the numbers annexed to hydrochloric acid really belong to nitric acid, and *vice versâ*. (*Vid. Ann. Chim. Phys.* 66, 243.)

ammoniac is added to a cold saturated solution of nitre, which by itself produces a deflection of 21°, the deflection increases to 26°; by the further addition of 1 part of sulphate of copper, it is raised to 30°. (Matteucci.)

A constant battery of eight pairs of amalgamated zinc, copper, and dilute nitro-sulphuric acid, gives the following deflections, all the solutions containing 1 part of salt in 100 parts of water: Pure water, $\frac{1}{2}$°; green vitriol, acetate of lead, or acetate of morphia, 2°; iodide of potassium or sulphate of copper, 3°; bicarbonate of potash, nitre, or chloride of calcium, 5°; bicarbonate of soda or nitrate of silver, 6°; carbonate of ammonia, 7°; carbonate of potash or soda, 8°; common salt, 10°; and sal-ammoniac, 12°. (Matteucci.)

The undermentioned salts give the following deflections, according as they are introduced into the current in a state of aqueous fusion or in saturated solution: Acetate of lead, 16° and 16°; chloride of calcium, 45° and 44°; alum, 42° and 42°; sulphate of zinc, 43° and 42°. Hence, the deflection is either the same in both cases, or rather stronger when the salt is in the fused state.—If a saturated solution of nitre gives 30°, and of chloride of potash 38°, fused nitre will give a deflection increasing from 42° to 55°,—and fused chlorate of potash, from 40° to 47°;—when solid matter begins to separate, the deflection increases to 55°. (Matteucci.)

A pair of zinc and copper plates excited by water sends a stronger current by means of copper-electrodes through dilute sulphuric acid, than a similar pair excited by dilute sulphuric acid sends through water.

Influence of the Temperature and Compression of the Electrolyte upon Decomposition.

Hot water is more abundantly decomposed by the electric current than cold water. (Gay-Lussac & Thénard.)—The deflection of the galvanometer increases considerably as the electrolyte is heated: but this increase reaches its limit at a certain temperature, which is so much the higher as the conducting power of the electrolyte is less. On subsequent cooling, the liquid still retains a little of the increased conducting power which it had acquired by heating. (Matteucci.)—In a larger volume of water exceeding an inch in diameter, the influence of heat is imperceptible. In dilute sulphuric acid, a very feeble current of 12° is increased to 30° by igniting both the electrodes, or only the negative one,—whereas heating the positive electrode alone has no effect whatever. Similarly with nitric acid, the deflection is increased from 12° to 80° by heating the negative electrode. (De la Rive.) [The application of heat to the negative electrode probably liberates the bubbles of hydrogen gas which cover that electrode in large quantities, and hinder the transference of electricity.]—The deflection of the needle is likewise increased by heating the positive electrode. (Faraday.)—Heating the positive electrode increases the current, only when the temperature is raised to the boiling point of the liquid—the heat then acting by mechanical agitation and removing from the negative electrode the substances (gas-bubbles) which have been carried towards it: hence the deflection is likewise increased by shaking the negative electrode. (Vorsselman de Herr, *Pogg.* 49, 109.)

The decomposition of water goes on in a sealed glass tube containing two platinum wires, even when the water is subjected by the accumulated *detonating gas* to a pressure of eleven atmospheres, the deflection of the

galvanometer even increasing a little under these circumstances. (Jacobi.) The development of gas still goes on when the water is subjected to a pressure of 150 atmospheres, till at length the tube bursts. (Degen, *Pogg.* 38, 454.)

Influence of the Relative Volume of the Electrolyte on Decomposition.

When the current from two pairs of zinc and platinum excited by dilute sulphuric acid, is conducted by means of two platinum plates into dilute sulphuric acid, the strength of the current is the same, whether the platinum plates are at the distance of six inches from one another or separated only by the thickness of a sheet of paper. (Faraday.) [With pure water, a greater difference would probably be found.]

The thinner the film of liquid which the current has to traverse, the greater is the deflection produced. The increase of deflection caused by diminishing the thickness of the liquid, is the more considerable as the conducting power of the liquid is less [*i. e.* as the resistance to the transposition of atoms is greater]. When, however, by enlarging the platinum plates, the current has been raised to its maximum, the deflection is no longer increased by bringing the electrodes nearer together. (Matteucci.)

The distance between the electrodes remaining the same, the deflection is augmented up to a certain point by increasing the height and breadth of the liquid; but when the increase in dimension is carried further, the deflection diminishes. The deflection is stronger when the positive electricity enters by the narrower part of the liquid, and the negative by the wider, than in the contrary case. (Matteucci.)

Influence of the Chemical Nature of the Electrodes on Decomposition.

The greater the tendency of the electrodes to combine with those elements of the liquid which are set free upon them, the more easily does the decomposition takes place.

If the quantity of electricity in the current of a single pair of zinc and copper plates in dilute sulphuric acid be equal to 1000 when the circuit is closed by good metallic conductors, it will amount to the following quantities when the current is conducted by the under-mentioned electrodes into the following liquids: zinc plates in water, 0·8; in fuming oil of vitriol, 64·7; in a mixture of 1 part of sulphuric acid and 3 parts water, 85·1;—platinum electrodes in hydrochloric acid, 2·6; in nitric acid, 17·7; in aqua regia, 338·3. Hence it appears that those liquids which do not act chemically on the electrodes offer the greatest resistance. (Fechner.)

If the cups *a*, *b* (*App.* 2), contain dilute sulphuric acid, *o* consisting of zinc, *p* of copper, and *g h i* of one of the following metals, no hydrogen gas is evolved at the end *p* when *g h i* consists of platinum, and only a trace when it is formed of gold; next follows silver, then copper, then tin, then iron, and lastly zinc, which yields most of all. If, however, the two cups contain ammonia, the deflection is stronger when *g h i* consists of copper than when it is formed of iron. (De la Rive.)

When the positive electricity of a pair of zinc and platinum is conducted by zinc into dilute sulphuric acid, the quantity of the current is the same as when the circuit is metallically closed without the interposition of a liquid. (Faraday: *vid.* 441.)

Influence of the Surface of the Electrodes upon Decomposition.

Electrodes of small surface evolve as much detonating gas from acidulated water in a given time as those of a larger surface. (Faraday.) When, however, the current is strong, the decomposition diminishes if the electrode be too small to allow free passage to the current; thus, a Daniell's battery of ten pairs yields 2·7 cubic inches of detonating gas, whether the electrodes are formed of broad plates of platinum, or of wires; but if the latter are covered with resin to within a quarter of an inch of their points, the quantity of gas per minute is reduced to 2·3 cub. in.; and when they are coated up to their points, it is only 0·8 cub. in.: in this last case, the gas is driven into the liquid with some force. (Daniell.) —With currents of small quantity, on the contrary, the decomposition is increased by diminishing the size of the electrodes, and thereby concentrating the current. (Wollaston, Matteucci.) The deflection is likewise stronger when the positive electricity enters by a narrower, and the negative electricity by a wider electrode, than in the contrary case [because a greater quantity of gas is evolved at the negative electrode]. (Matteucci.)

Decomposition of Individual Compounds.

Nicholson and Carlisle discovered the decomposition of water, Hisinger & Berzelius that of salts, Sir H. Davy that of the alkalis.

Water.

The electric current acts more readily on water contained in a bundle of asbestus fibres than on a column of that liquid of equal length and thickness in a U-tube. (H. Davy.)

Many substances which are soluble in water favour its decomposition (p. 443); but with a powerful battery, the same quantity of detonating gas is obtained in a given time, whether the water is mixed with a large or a small quantity of sulphuric acid, or holds in solution, potash, soda, carbonate of potash, sulphate of ammonia with excess of ammonia, or sulphate of soda. Dilute sulphuric acid of sp. gr. from 1·25 to 1·336 is best adapted for the purpose. Acid of 1·495 sp. gr. yields a somewhat greater quantity of gas, because it retains less oxygen gas in solution. With acid of still greater strength, *e. g.* 2 measures of oil of vitriol to 1 measure of water, only 0·57 volume of oxygen gas is obtained for every 2 volumes of hydrogen,—possibly because the predisposing affinity of the sulphuric acid favours the production of peroxide of hydrogen. (Faraday.) Connell likewise obtained with these different solutions, and also with that of boracic acid, constantly the same quantity of detonating gas.

When water is divided by a membrane into two portions, and one of the electrodes of a powerful battery immersed in each of them, the water rises in the negative and sinks in the positive division. (Porret.)—This effect is exhibited by distilled water and rain-water, which are bad conductors, but not by saline solutions,—and is due to the resistance which the water opposes to the passage of positive electricity. (De la Rive.)—On the contrary: This effect is seen only in water which holds in solution some salt, by the decomposition of which, alkali collects in the negative and acid in the positive division; and the rise of the water is not a

direct consequence of the action of the electric current, but is produced by endosmose. (Dutrochet, *Pogg.* 28, 36; *comp.* Schweigger, *Schw.* 16, 383.)

Water not freed from atmospheric air yields, in consequence of the nitrogen which it contains, nitric acid in the positive gold cup, and ammonia in the negative gold cup connected with the former by means of asbestus,—the nitrogen combining with oxygen at the anode and with hydrogen at the cathode: the quantity of the nitric acid continually increases, but that of the ammonia soon reaches a maximum. If the receiver under which the gold cups are placed be exhausted of air, then filled with hydrogen, and again exhausted, neither acid nor ammonia appears in the water. (H. Davy.)

When platinum electrodes are used, somewhat less than one measure of oxygen gas is obtained for every two measures of hydrogen; for the former is more readily absorbed by water,—partly because it is evolved in smaller bubbles, partly because water is essentially capable of absorbing oxygen gas in greater quantity than hydrogen; perhaps also a small quantity of peroxide of hydrogen is formed at the anode. The detonating gas likewise contains nitrogen, which was previously dissolved in the water. (Faraday.)—Just at the commencement of the decomposition, the detonating gas contains less than its normal quantity of oxygen, because the positive platinum wire oxidates on the surface: the latter portions of detonating gas contain almost exactly the proper quantity of oxygen. If both the platinum plates have been previously cleansed (by rubbing them while hot with hydrate of potash, dipping them in oil of vitriol, and washing with water out of contact of air), the negative plate immediately evolves gas, the positive plate not till after some few seconds, because the first portions of oxygen are retained by the platinum: if, on the other hand, the platinum plates have been exposed to the air for some time, gas is immediately disengaged on the positive plate, but often not till after twenty seconds on the negative plate,—because the first portions of hydrogen set free have to reduce the oxide of platinum. (De la Rive.)

Clean platinum wire used in rapid alternation as positive and negative electrode becomes covered with a black powder, consisting of finely divided metallic platinum; for the metal, in conducting positive electricity, takes up a trace of the liberated oxygen and forms an oxide, which, when afterwards used as a cathode, is reduced by the hydrogen to the state of finely divided platinum.—If the electrode *a* consists of a thin platinum wire, and the electrode *b* of a broad plate of the same metal, the volumes of oxygen and hydrogen gas evolved from water acidulated with sulphuric acid are in the exact proportion of 1 : 2, when *a* is used as the anode,—because the small surface of the wire can take up but a trifling quantity of oxygen; but when *b* is used as anode, the quantity of oxygen is deficient; and if *b* be then put in the place of the cathode, the quantity of hydrogen appears deficient, because a portion of that element is employed in reducing the oxide previously formed on *b*. Hence, when platinum which has been used as anode is afterwards made to conduct negative electricity, some seconds elapse before hydrogen gas appears on its surface, because the first portions enter into combination with the oxygen of the oxide of platinum. This power possessed by platinum of fixing oxygen on its surface explains the fact announced by Peclet, viz. that platinum may be positive with regard to gold. Gold wire used as the anode in dilute sulphuric acid acquires a reddish tinge from oxidation, —and, when the poles are changed, becomes pulverulent on the surface, in

consequence of reduction of the gold previously oxidized. (De la Rive, *Pogg.* 46, 489; and more fully in *Pogg.* 54, 378.)

To subject a liquid to the action of rapidly alternating currents, Clarke's magneto-electric apparatus may be used (or Daniell's constant battery with a *Commutator*). To determine the quantity of the current, a Breguet's thermometer may be interposed in the circuit. The less the current is retarded by the liquid and electrodes, the higher will be the temperature, = T. The liquids experimented upon are: 1 measure of oil of vitriol to 9 measures of water = V, and 1 measure of concentrated nitric acid to 9 measures of water = N. The quantity of mixed hydrogen and oxygen gases evolved in the constant interval of five minutes = G. The residue obtained after the successive detonation of all the several quantities of gas = R. The results are as follows:

Two platinum wires in N give, at the beginning, 1·5 cub. in. G (in 5 minutes), T = 20°; after 20 minutes, 0·7 cub. in. G (in 5 minutes); T = 33°; after 40 minutes, only 0·05 cub. in. G, and soon afterwards, all evolution of gas ceases; T = 35°. The wires become completely covered with black powder, consisting of finely divided platinum. The whole quantity of gas obtained amounts to 7 cubic inches; and after explosion there remains 0·65 cub. in. R, which is a mixture of oxygen and nitrogen: the latter probably arises from air contained in the water,—the former from the nitric acid having exerted a slight oxidating action on the platinum, and hydrogen having been expended in the reduction of the oxide thus formed.

Platinum wires in V: In the first 5 minutes, 1·4 cub. in. G; after 40 minutes, 0·5; T = 50°. After explosion, there remains 0·3 cub. in. R, consisting of 0·15 cub. in. of hydrogen gas and 0·15 cub. in. of nitrogen. The excess of hydrogen is due to the oxidation of the platinum.

Gold wires in N: In the first 5 minutes, 1·5 cub. in. G; T = 21; after 40 minutes, 0·9 cub. in. G; T = 27°. When the experiment is continued for a longer time, the evolution of gas no longer diminishes, and T no longer increases. R amounts to 0·4 cubic inches, consisting of 0·2 oxygen gas and 0·2 nitrogen; when the experiment is continued, R does not increase any further.

Gold wires in V: At first, 1·1 cub. in. G; after 40 minutes; almost 0 G; T = 44°; 0·22 cub. in. R consisting of 0·16 hydrogen and 0·06 nitrogen.

Silver wires in V give no perceptible evolution of gas; T = 50°.

Copper wires in V evolve gas at intervals, and generally in very small quantity, probably nothing but hydrogen; T varies from 43° to 46°, according as more or less gas is evolved. The wires oxidate slightly, and acquire a pulverulent surface, while a portion of oxide of copper dissolves in the acid. Gold and silver wires likewise acquire pulverulent surfaces.

Lead wires in V: In the first five minutes; 0·5 cub. in. hydrogen gas, T varying from 5° to 6°. The liquid is rendered turbid by a white powder [sulphate of lead?], with which also the anode becomes covered and consequently isolated; hence the small rise of temperature.

Iron wires which evolve 0·35 hydrogen gas from V without the aid of electricity, give in the electrie current 10 cub. in.; T = 33°.

Cadmium wires in V give scarcely any gas without the aid of the current, and no more when placed in the current.

Zinc wires give about the same quantity of gas with and without the current.

The smaller, therefore, the evolution of gas, and the more the passage of the current is facilitated by oxidation and deoxidation, the higher is the temperature produced, and the greater, therefore, the quantity of electricity which passes through. The higher the temperature shown by the Breguet's thermometer, the colder does the liquid remain. (De la Rive, *Pogg.* 54, 497.)

[When once a sufficient quantity of finely divided platinum has been formed, the evolution of gas ceases, because the platinum in this state readily takes up the oxygen separated from the water by the action of the current,—and while one wire is oxidized in this manner, the other is deoxidized by the hydrogen: the opposite current which immediately succeeds, reverses the process—and so on. The current has now no further decomposition to effect, which is not immediately compensated by the formation of a new compound, and therefore its whole force is expended in transposing the atoms. Hence, as the evolution of gas diminishes, the current increases in quantity, and heats Breguet's thermometer more strongly; and as the decomposition of the water ceases, the rise of temperature in the liquid which accompanies this decomposition, ceases also. The case is similar with the other metals.]

Charcoal used as the anode in the decomposition of water acidulated with sulphuric acid, evolves carbonic acid and carbonic oxide gases. (Faraday.)

Antimony used as an anode in water, becomes covered with suboxide.

When mercury is placed under water acidulated with sulphuric acid, and the platinum cathode dipped into the mercury, while the anode is immersed in the water, the negative wire becomes quickly amalgamated; and the mercury, which has thus been made to act for a time as the cathode, has the power, when taken out of the circuit, of quickly amalgamating wires of platinum, iron, or steel. This effect is due to a trace of an alkali-metal [or hydrogen] which the mercury has taken up by electrolytic action. (Grove.)

Tellurium acting as cathode in water generates telluretted hydrogen, which dissolves and is again decomposed by the oxygen separated at the anode, the tellurium being precipitated in brown flakes; hence the quantity of oxygen evolved is but small. (Magnus.)—When sulphur or selenium is attached to the platinum cathode, a yellow precipitate of sulphur or a red precipitate of selenium is obtained, sulphuretted or seleniuretted hydrogen being first formed and then decomposed by the oxygen, which would otherwise escape at the anode. (Magnus, *Pogg.* 17, 521.)—Antimony acting in water as cathode, is said by Ruhland to yield a brown-black compound of antimony and hydrogen.

Development of an Odorous Substance in the Decomposition of Water.

The decomposition of water is attended with the production of a peculiar odour, which is confined to the positive electrode, so that when the hydrogen and oxygen gases are collected in separate vessels, the latter only is affected with the odour. The odorous principle is developed only when gold or platinum is used as the anode; not with oxidable metals or charcoal. The odour is perceived when the water holds in solution, phosphoric acid, sulphuric acid, nitric acid, nitre, phosphate of potash, or sulphate of soda; not when it contains hyponitric acid, hydrochloric acid, hydrobromic acid, metallic iodides, bromides, or chlorides, or protosulphate of iron; it is only occasionally observed in aqueous solution of

potash, never in nitric acid, either concentrated or of the ordinary strength; it is not evolved when the aqueous solutions are heated; it is strongest in sulphuric acid diluted with six times its weight of water. The odour in its concentrated state is powerfully sulphureous; when diluted, it resembles that of phosphorus. Both the oxygen when collected separately, and the mixed gases collected together, possess the odour, and retain it when kept in well-stopped vessels.

The oxygen gas, when collected in a bottle, quickly loses its odour by contact with a small quantity of powdered charcoal, arsenic, antimony, bismuth, or filings of zinc, tin, lead, or iron; most quickly by contact with charcoal and iron. The odour is likewise destroyed by small quantities of the solution of hyponitric acid, protochloride of tin, and protochloride or protosulphate of iron; likewise by heated gold or platinum. But cold platinum or gold leaf held in odorous oxygen gas becomes negative towards other portions of platinum or gold, when connected with them by means of the galvanometer and immersed in any watery liquid. The current is strong but soon ceases. The metals retain this negative state in air for some hours, but lose it in a few seconds when immersed in hydrogen gas, and become positive when kept in that gas for a longer time. Copper also exhibits this effect, but in a slighter degree. When the odour of oxygen gas has been destroyed by any of the above methods, gold or platinum no longer becomes negative in it.

This same odour is perceptible after a stroke of lightning, and likewise when an electrical machine is being used. By the electrical machine also, platinum and gold—and likewise copper in a slight degree—may be rendered negative, the metal being held for a few turns of the machine at about an inch distance from the blunt end of a rod inserted into the conductor, so as to expose it to the positive electricity issuing therefrom, or else exposed to the negative electricity given out from the rubber. Platinum does not become negative when the point of the conductor or the platinum itself is hot or damp, in which case no smell is perceptible,—neither is the negative state induced when the platinum itself is attached to the conductor, and forms the point from which the electric fluid issues.

The odorous principle must be a gas analogous to chlorine or bromine. It is either an oxide of hydrogen, containing more oxygen than the peroxide commonly so called (this hypothesis is perhaps the least hazardous), or it is a simple substance, *Ozone*, which perhaps exists in combination with hydrogen in water, and likewise in the aqueous vapour of the air, and is liberated at the same time that the water is decomposed. (Schonbein, *Pogg.* 50, 616.)

With a feeble battery, no odour is perceptible if the anode consists of a large plate of platinum; but a strong odour is emitted when the anode is formed of a platinum wire coated up to the point with wax. When, from long-continued action of the current, the acidulated water becomes very hot, the odour ceases to be emitted, but a black powder makes its appearance, consisting of finely-divided platinum separated by the electric current. The odour varies a little according to the nature of the metal of which the anode consists; with platinum and silver, it is sharper and more unpleasant than with gold; with copper, it is feebler and of a different character. The odour is due to finely-divided metallic oxide, diffused through the liberated oxygen gas. The electric spark likewise contains finely-divided metallic particles separated from the conductor, and substances in a state of minute division are found in the track of a stroke of lightning. (De la Rive, *Pogg.* 54, 402.)—When silver and other

metals are burnt in the oxygen gas blowpipe, in which case the oxide rises in a state of minute division, no phosphoric odour is emitted. (Gm.)

Peroxide of hydrogen (HO^2) is gradually resolved into oxygen gas—in greater quantity than that yielded by water—and hydrogen gas. (Thénard.) [Supposing no water to have been mixed with the peroxide, this experiment must be regarded as testifying against Faraday's law. (p. 434.)]

Aqueous Solution of Iodine, Bromine, or Chlorine.

Iodine and bromine facilitate the decomposition of water—without being themselves transferred to either of the poles—apparently by combining with the hydrogen liberated from the water. Solution of bromine yields a mere trace of hydrogen gas at the negative pole; with solution of iodine, the quantity of hydrogen obtained is three-fourths as great as that collected in a voltameter interposed in the circuit. (Connell.)—Balard (*J. pr. Chem.* 4, 167) likewise obtained from aqueous solution of bromine, hydrobromic acid at the negative pole, but no bromic acid at the positive: chlorine water, on the contrary, yielded hydrochloric acid at the negative, and a little chloric acid at the positive pole.

When bromine is added to a solution of starch turned blue by iodine, a yellowish mixture is produced. This mixture, subjected to the action of the current, turns blue at the negative and orange-coloured at the positive pole. Hence iodine is transferred to the former, bromine to the latter. (De la Rive, *Ann. Chim. Phys.* 35, 164.)

Aqueous solution of oxide of chlorine (ClO^4) yields hydrogen at the cathode, and a small quantity of oxygen gas and perchloric acid (ClO^7) at the anode. (Count Stadion.)

Aqueous Oxygen-acids.

On filling a U-tube completely with dilute *Phosphoric acid*, tying over both ends with bladder, fixing each of them into the perforated bottom of a separate glass-vessel filled with the same dilute solution of phosphoric acid, conducting into both glasses the current of a constant Daniell's battery, and determining at the same time the volume of oxygen and hydrogen gases evolved,—it is found that while one atom of water is decomposed, only from one-fifth to one-fourth of an atom of phosphoric acid has been carried over to the positive glass. (Daniell.)

An iron wire serving as the anode does not dissolve in dilute phosphoric acid; but, like platinum, it develops oxygen gas when the circuit is ultimately closed with it. On the contrary, it oxidizes and dissolves when immersed before the rest of the circuit is closed, because in this case chemical action precedes that of the electricity.—Iron used as an anode in aqueous hypophosphorous or phosphorous acid develops no oxygen, possibly because phosphoric acid is formed. (Schönbein.)

Concentrated phosphoric acid produces a metallic phosphuret on a cathode consisting of copper or platinum. (H. Davy.)

Common hydrate of phosphoric acid yields merely oxygen and hydrogen gas, without sensible precipitation of phosphorus. (Faraday.)

Dilute Sulphuric acid. If two cups *a*, *b*, connected by asbestus, contain dilute sulphuric acid, and the two following cups, *c*, *d*, likewise connected by asbestus, contain solution of sulphate of soda, the quantity of sulphuric acid in which is the same as that in *a b*,—then, on connecting

platinum wire, and dipping the positive wire into *a* and *d*, it is found after a time that while $\frac{1}{16}$ of the sulphuric passes from *c* into *d*, the quantity which passes from *a* to *b* is from $\frac{1}{11}$ to $\frac{1}{12}$. Hence it appears that the greater affinity of ric acid facilitates its passage to the positive pole. (Faraday.)

In the apparatus for phosphoric acid, described on page 451, only from fifth to one-fourth of an atom of sulphuric acid goes over into the ive cup for every atom of water decomposed, and this is the case ever may be the degree of dilution, and whether the anode consists atinum, copper, or zinc. (Daniell.)

In dilute sulphuric acid, iron acts as the positive conductor, just as in ric acid. (Schönbein.)

With electrodes in dilute sulphuric acid consist of copper, little gas is evolved at the anode, the copper oxidizing and dis- the solution acquiring a blue colour. The cathode yields which gradually diminishes in quantity, but does not enti even after several days; at the same time, metallic copper in a moculeus state, and of a brown-red colour, is deposited at the cathode. (Jacobi.)

Oil of vitriol impedes the current much more than dilute sulphuric acid, fing oxygen gas at the anode, and sulphur, together with hydrogen from sulphur, at the cathode. (Faraday.)—Zinc, copper, or brass, as the anode, becomes covered with a non-conducting sulphate, impedes the current in such a manner, that on touching the oil of with a conductor, only the negative electricity of the battery is wn: hence the oil of vitriol acts as a unipolar conductor. When e is formed of lead or tin, the current continues,—because the sul- phates of those metals dissolve in the oil of vitriol; silver, gold, or plati- num as the anode also gives a continuous current, because no sulphate is produced. (Ohm, *Schw.* 59, 385.)

Aqueous solution of Sulphurous acid **yields oxygen gas and sulphuric acid at the positive pole, hydrogen gas and sulphur at the negative pole. The quantities of oxygen and hydrogen actually evolved are less than in a voltameter placed in the same circuit, because part of the oxygen is expended in oxidizing the sulphurous acid, and part of the hydrogen in reducing the sulphur. The decomposition is facilitated by the addition of a small quantity of sulphuric acid. (Faraday.)**

Aqueous solution of Iodic acid. **A solution of 1 part of iodic acid in 10 parts of water yields oxygen gas at the anode, equal in quantity to that in the voltameter, and iodine at the cathode without any hydrogen. Consequently, the water alone is directly decomposed, and its hydrogen separates iodine at the cathode. (Connell.)**

Hyponitric acid, prepared from nitrate of lead, conducts and decom- poses slowly,—but water appears to be present. (Faraday.)

Nitric acid. **Very strong nitric acid conducts well, and yields oxygen gas at the anode; at the same time it turns yellow and afterwards red at the cathode, and ultimately evolves nitric oxide gas. The same acid diluted with its own or a larger quantity of water, gives hydrogen gas at the negative pole, the quantity increasing with the strength of the cur- rent and the dilution of the acid. The quantity of oxygen gas obtained from either strong or weak acid is the same as that in the voltameter; so likewise is the quantity of hydrogen, if the specific gravity of the acid be not eater than 1·24. Hence it is only the water that is directly decomposed the current, the hydrogen liberated from the water abstracting oxygen**

from the acid, when not too dilute, and thus reducing it to the state of nitrous acid and nitric oxide. (Faraday.)

When the current of a small cup-apparatus of sixteen pairs is sent through nitric acid of 1·49 sp. gr. the negative platinum wire evolves hydrogen gas for a moment,—after which, all evolution of gas ceases, and nitrous acid is produced. The more dilute the acid, the longer does the evolution of gas continue; in a mixture of one measure of acid and one of water, it lasts for half a minute; in a mixture of one measure of acid and two of water, it goes on uninterruptedly. The thicker the wire, the sooner does the evolution of gas terminate. By the following methods, platinum wire may be brought into a peculiar condition, in which, if it be placed in an acid of such a strength that the evolution of gas would cease after a while, it will evolve no gas even from the beginning:—1. By placing the two polar wires in immediate contact, dipping them thus united into the acid, and then suddenly separating them. (In this case, however, the acid must be diluted with somewhat less than one measure of water.)—2. By igniting the negative wire, and immersing it after the positive wire.—3. By communication: If the negative wire, after it has ceased to cause evolution of gas in the acid, be joined outside the liquid with another platinum wire, then the latter wire immersed and the former withdrawn, the second wire will evolve no gas either at first or afterwards; moreover, the same property may be communicated from this to a third wire—and so on.—A wire which has lost the power of liberating hydrogen gas recovers it by exposure to the air. The time of exposure must be longer as the strength of the acid is greater. In the case of acid diluted with an equal bulk of water, momentary exposure to the air is sufficient; in this case, it is likewise sufficient to interrupt the current for a moment. Sometimes, again, the same effect is produced by agitating the wire in the acid.

In these experiments, the platinum wire perhaps favours the combination of hydrogen with the oxygen of the nitric acid, in the same manner as it acts in detonating gas.—With a stronger electric current, the evolution of gas at the cathode takes place uninterruptedly, because the water is decomposed too rapidly to allow the preceding effects to take place. (Schönbein.)

Iron used as an anode in dilute nitric acid behaves in the same way as in phosphoric or sulphuric acid, retaining its passive condition with even greater facility. (Schönbein.)

When platinum wire is used as the cathode and active iron wire as the anode, in a small cup-apparatus, the latter being first immersed in nitric acid of 1·35 sp. gr., and then the circuit closed, the iron continues to dissolve and evolves no oxygen gas. If, on the contrary, the circuit be closed in such a manner that the iron wire is last immersed, the iron becomes passive and evolves oxygen gas just as platinum does, while nitrous acid is formed at the cathode. If the acid be diluted with from 20 to 400 measures of water, then under the same circumstances two measures of hydrogen gas are evolved at the surface of the platinum for every measure of oxygen evolved at that of the iron. If, however, the two wires be made touch within the liquid, the evolution of oxygen ceases and does not recommence when they are separated. In a mixture of one measure of acid and 10 of water, the evolution of oxygen on the iron likewise ceases on taking the platinum wire out of the acid for a few seconds, and then dipping it in again. It is only when the acid is very dilute, that evolution of oxygen recommences some time after the closing of the cir-

cuit.—When the negative platinum wire which liberates hydrogen gas from dilute nitric acid, is replaced by an iron wire, no further evolution of hydrogen takes place. Iron which has been rendered passive by nitric acid in any way whatever remains passive when used as an anode, even in the most dilute acid, provided that the circuit be finally closed by the iron; (if, on the contrary, it is immersed in the acid before all the other parts of the circuit are connected, it dissolves continuously.) The existence of this passive condition in nitric acid, of a degree of dilution at which it easily dissolves peroxide of iron, is unfavourable to the supposition that the peculiar condition of passive iron arises from the formation of a film of oxide. [By the action of the current the iron is immediately surrounded with concentrated acid.] While the current continues, no gradual solution of the passive iron (such as is asserted by Faraday) can be perceived, even after several hours; but as soon as the current is interrupted, the wire begins to dissolve: hence the passive state is directly produced by the current [which causes concentrated acid to accumulate round the iron].—When dilute nitric acid is disposed in a layer above solution of potash in any vessel, and the positive iron wire is dipped through the acid into the potash, and then the platinum cathode immersed, the portion of iron wire which dips into the potash becomes oxidated, as well as that which is immersed in the acid. (Schönbein.)

When iron is used as the anode of a battery of 20 pairs in nitric acid of specific gravity from 1·47 to 1·5, it liberates oxygen but gradually dissolves, even when completely immersed in the acid, and connected by means of a platinum wire with the positive pole of the battery. If the circuit be then unclosed, the iron becomes covered with a black coating of insoluble oxide. Passive iron used as the anode in a mixture of nitric and sulphuric acid liberates oxygen gas. (Andrews.)

The gas evolved from nitric acid, either concentrated or moderately diluted, at the iron anode of a strong battery, is not oxygen but nitric oxide; that evolved in a similar manner from acid 30 times diluted, is nitrous oxide. From this it follows that the iron is oxidized by the nitric acid, although it retains its metallic lustre. (Buff.)

Tin used as an anode in strong nitric acid remains permanently passive, and stops the passage of the current more effectually than iron or bismuth. (Andrews.)—According to Buff, on the contrary, tin exhibits the same behaviour as that which he observed in the case of iron.

Zinc used as an anode dissolves in strong nitric acid, but much more slowly than when the current ceases. (Andrews.)

Bismuth when it forms the anode is attacked by nitric acid as strongly as when not placed in the circuit. (Schönbein.)—When the current proceeds from two pairs of amalgamated zinc and platinum, and the platinum capsule containing nitric acid of sp. gr. 1·4 is connected with the negative pole, the solution of the bismuth immediately ceases,—and on breaking the circuit, the metal is found to have been rendered passive. If, on the contrary, the current is excited by a battery of 20 pairs, the bismuth dissolves continually though slowly, and seldom appears passive after the circuit is broken. (Andrews.)

When copper wire forms the anode in a mixture of nitric and sulphuric acid, the galvanometer after the first instant shows but a very feeble current—the decomposition of the liquid ceases entirely—the copper wire liberates no gas—is not attacked—and when the circuit is broken it is no longer soluble in the nitro-sulphuric acid (in which likewise active copper dissolves but slowly); at the same time, it

appears bright on the surface. It appears then that the copper becomes covered with an insulating film. (Grove, *Phil. Mag. J.* 15, 392; abstr. *Pogg.* 49, 600.)

Fused *Arsenic acid* containing water neither conducts nor suffers decomposition. (Faraday.) Aqueous solution of arsenic is rapidly decomposed, with abundant deposition of arsenic at the cathode. Aqueous *Arsenious acid* is decomposed in the same manner, but more slowly. (Bischof, *Kastner. Archiv.* 6, 438.) [Was not arseniuretted hydrogen evolved at the same time?]

Aqueous solutions of Hydrogen-acids.

These acids evolve hydrogen at the negative pole and the radical at the positive pole: the latter often combines with the metallic electrode, but is set free when graphite is used as the anode.

Hydriodic acid, whether concentrated or dilute, yields the same quantity of hydrogen gas at the negative pole; and this quantity corresponds to that collected in the voltameter interposed in the same circuit. But the concentrated acid gives only iodine at the positive pole; the dilute acid gives less iodine, but oxygen gas with it. In the former case, hydriodic acid alone is decomposed; in the latter, less of the acid but water besides. (Faraday.) The more dilute the acid and the stronger the current, the greater is the quantity of oxygen gas obtained. (Matteucci.)

Aqueous *Hydrobromic acid* is resolved into hydrogen at the negative pole, and bromine, which dissolves, at the positive pole.

Concentrated *Hydrochloric acid*, or a mixture of it with at most 8 measures of water, evolves hydrogen at the negative and chlorine at the positive pole; a small portion of the chlorine combines with the platinum of the anode. A mixture of 1 measure of strong hydrochloric acid with 9 measures of water evolves a little oxygen together with the chlorine; and from a mixture of 1 measure of strong acid with 100 measures of water, 17 measures of oxygen gas are evolved for every 64 measures of hydrogen; consequently, 30 measures of chlorine must be set set free at the same time. In this case, the quantity of hydrogen is constant, whatever may be the degree of dilution of the acid. Hydrochloric acid seems to be more inclined to decomposition than water, since it is only when the acid is very much diluted that water is decomposed at the same time. (Faraday.)—Greater intensity of the electric current likewise increases the quantity of oxygen gas. (Matteucci.)—When the anode consists of gold, silver, copper, iron, &c., a chloride of the metal is formed—and, unless it be chloride of silver, dissolves in the surrounding liquid.

Passive iron forming the anode in aqueous solutions of hydracids, such as hydrochloric acid, is always dissolved, in whatever manner the circuit may be closed. (Schönbein.)

Anhydrous *Hydrofluoric acid* yields hydrogen gas at the negative pole, whilst the positive platinum wire is corroded by the formation of a brown substance, probably fluoride of platinum. (H. Davy.)—The hydrated acid is not decomposed, only the water with which it is united suffering decomposition. (Faraday.)

Hydrated *Hydrocyanic acid* gives passage to the current with difficulty,—more readily however when a small quantity of sulphuric acid is added to it. In both cases, the normal quantity of hydrogen gas is

obtained at the negative pole, whilst cyanogen dissolves in the liquid at the positive pole—as was formerly shown by Gay-Lussac. (Faraday.)

Hydrated *Sulphocyanic acid* and *Ferrocyanic acid* behave like hydrocyanic acid. (Faraday.)—Sulphocyanic acid accumulates undecomposed at the positive pole. (Porret.)

According to Faraday's and Matteucci's hypothesis, the hydracids are directly decomposed; but according to Connell, it is only the water mixed with them that suffers direct decomposition, the oxygen separated at the anode combining with the hydrogen of the acid which it there meets with, and setting the radical free. But the experiments on which he founds his opinion are by no means satisfactory.

Metallic Sulphurets, Iodides, Bromides, Chlorides, Cyanides, Sulphocyanides and Ferrocyanides.

Fused *Liver of Sulphur* yields potassium at the cathode. (Jaquin, *Gilb.* 28, 338.)—The *yellow solution of Sulphuret of Potassium* (p. 375) yields a quantity of sulphur at the anode and hydrogen gas at the cathode. (Faraday.)—Fused *Sulphuret of Silver* is decomposed, to a slight extent, into sulphur at the positive and silver at the negative pole.

Fused *Iodide of Potassium*, or *Iodide of Lead*, is resolved into iodine at the anode and metal at the cathode.—Aqueous solution of iodide of potassium yields iodine at the anode, potash and hydrogen gas at the cathode, water being decomposed by the potassium there separated. (Faraday.)—Fused *Chloride of Lead* yields lead at the cathode, chlorine at the anode: when the latter consists of graphite, chlorine is set free; but when it consists of platinum, part of the chlorine combines with the platinum, and chloride of platinum becomes mixed with the chloride of lead. (Faraday.)—Fused *Protochloride of Tin* is resolved into metallic tin and bichloride of tin, the latter escaping in vapour. (Faraday.)—Fused *Chloride of Silver* is resolved into silver and chlorine: when the electrodes are formed of silver, the anode loses as much silver as the cathode gains, and no chlorine is evolved. (Faraday.)—Fused *Protochloride of Mercury* conducts, and appears to be decomposed; disturbing causes are however present. (Faraday.)—Fused *Terchloride of Antimony* conducts badly and is but little decomposed, perhaps only on account of the presence of a small quantity of water. (Faraday.)

Aqueous solution of *Sal-ammoniac* is resolved into chlorine at the positive and hydrogen gas and ammonia at the negative pole. [This accords with the ammonium theory of Berzelius, according to which sal-ammoniac is not $N H^3$, H Cl, but $N H^4$, Cl. The result may, however, be explained on the former hypothesis; supposing namely that the current decomposes hydrochloric acid into hydrogen at the negative and chlorine at the positive pole, and that the ammonia which has been deprived of its hydrochloric acid, is set free at the negative pole.] Solution of sal-ammoniac with silver electrodes gives both hydrogen and oxygen gases, the latter however not in sufficient quantity; the positive wire becomes covered with chloride of silver, and the liquid in the neighbourhood of the negative pole is found to contain free ammonia. When iron wires are employed, gas is evolved only at the negative wire; it gradually however diminishes in quantity as the wire becomes covered with crystalline reduced iron. The positive wire is corroded and oxide of iron separates. The liquid on the negative side is found to contain

ammoniuret of protoxide of iron besides sal-ammoniac. (Hisinger & Berzelius.)

If a cup formed of sal-ammoniac be wetted, then placed upon a piece of platinum foil connected with the positive pole of the battery, and filled with mercury into which the platinum wire of the negative pole is made to dip, chlorine is developed at the positive platinum plate, and the mercury swells up in the state of ammoniacal amalgam ($Hg + N H^4$) to 5 times its original volume, its vegetations at the same time penetrating into the sal-ammoniac. When the circuit is broken, the amalgam immediately runs together in the form of liquid mercury. (H. Davy, *Gilb.* 33, 247.)

Solution of Common Salt gives chlorine at the positive, hydrogen gas and soda at the negative pole. The salt is probably first resolved into chlorine and sodium, and the sodium oxidized by the water; for when the cathode consists of mercury, sodium-amalgam is obtained. (Higgins & Draper, *N. Edin. Phil. J.* 14, 314.)—Common salt, in which silver wires are immersed, evolves gas only at the negative wire at first, but afterwards at the positive wire also: the latter becomes covered with chloride of silver; the liquid surrounding it contains in solution chlorine and a compound of silver not precipitable by chlorine; the liquid on the negative side contains free soda.—When lead wires are used, the negative wire alone evolves gas, and subsequently becomes covered with fine crystals of lead; the positive wire acquires a coating of chloride of lead. A positive wire formed of iron or zinc likewise evolves no gas, but dissolves in the state of metallic chloride, from which a film of oxide is precipitated at the surface of contact of the chloride with the alkaline liquid on the negative side. (Hisinger & Berzelius.)

A globule of mercury immersed in solution of *Chloride of Barium* and connected with the negative pole of a feeble battery, forms solid vegetations of barium-amalgam. (Herschel.)—In solution of *Chloride of Calcium* the negative wire alone yields gas, and becomes covered, first with a white crust, then also with needles of lime (hydrate) which first diminishes the evolution of gas, and then stops it altogether. The positive wire dissolves as chloride of iron, and the solution deposits protoxide of iron at the surface of contact of the latter with the calcareous liquid. (Hisinger & Berzelius.)

From a solution of *Protochloride of Iron*, black magnetic oxide of iron is deposited at the negative pole. (H. Davy,—according to Becquerel, it is deposited in small grains.)—A concentrated solution of *Chloride of Copper* or *Chloride of Gold* in water gives, when subjected to a feeble electric current, merely metal at the negative pole without any hydrogen gas: the gas is however evolved from a dilute solution when acted upon by a strong current. Hence it appears that water is less decomposible than these metallic chlorides,—and the order of decomposibility is: iodide of potassium, hydriodic acid, hydrochloric acid, metallic chlorides, water acidulated with sulphuric acid. (Matteucci.)

Iron acting as anode in solutions of metallic sulphurets, iodides, bromides, chlorides, and fluorides, dissolves, even when the circuit is not closed before the immersion of the iron. (Schönbein.)

Aqueous solutions of *metallic Fluorides* are decomposed with separation of fluorine at the anode. (Faraday.) When the electrodes are immersed in two cups of fluor-spar, filled with water and connected by fibres of asbestus, lime-water is found after two days in the negative cup, and hydrofluoric acid in the positive cup. (H. Davy.)

Aqueous solution of *Cyanide of Potassium* yields hydrogen gas and potash at the cathode: no oxygen is evolved at the anode, but the liquid turns brown. Fused cyanide of potassium is likewise decomposed. Solutions of metallic *Sulphocyanides* and *Ferrocyanides* behave in a similar manner. (Faraday.)

Alkalis and Earths.

Concentrated solution of *Ammonia* conducts as slowly as pure water; by the addition of a small quantity of sulphate of ammonia, it is rendered more easily decomposible. In this case it yields hydrogen gas at the cathode equal in quantity to that collected in the voltameter, and nitrogen gas at the anode, frequently mixed with a small and variable quantity of oxygen gas. Hence for each measure of gas at the anode, three or four measures are evolved at the cathode. When gold electrodes are used, the positive wire dissolves, and becomes covered with amber-coloured fulminate of gold, whilst metallic gold is deposited on the negative wire. Concentrated solution of ammonia, with iron electrodes, yields hydrogen gas at the negative, and pure nitrogen at the positive pole. On the third day, the anode begins to acquire a coat of oxide. If the ammonia be mixed with three times its volume of water, hydrogen and oxygen gas are evolved, the latter however in smaller quantity, because the iron suffers corrosion. (Hisinger & Berzelius.)

When solution of ammonia is placed in a tube over mercury, which is connected by a platinum wire with the negative pole, whilst the platinum wire of the positive pole dips into the ammonia, oxygen gas is evolved at the positive wire; and the mercury, which does not at first evolve any gas, is converted into a thickish mass of ammoniacal amalgam (a compound of mercury with $N H^4$), which spreads out in vegetations, and swells up to six times the original volume of the mercury. As soon as this amalgam comes in contact with the positive wire, it is partially decomposed with a hissing noise, and shrinks up, then grows up again till it reaches the positive wire, when it is once more decomposed—and so on. Breaking the circuit likewise decomposes the amalgam with violent evolution of hydrogen gas. (Berzelius & Pontin, *Gilb.* 36, 260.)

Hydrate of Potash, slightly moistened and subjected to the action of a powerful battery, yields oxygen gas at the anode, and at the cathode hydrogen and gas and potassium: the metal adheres in globules to the platinum wire, and then burns. *Hydrate of Soda* behaves in a similar manner. (H. Davy.)

Moistened *Hydrate of Baryta, Strontia, Lime, or Magnesia*, is not decomposed by the current even of a powerful battery, unless the action be assisted by the affinity of mercury for the metal contained in these bases. But if either of these hydrates be formed into a cup, the cup placed on a plate of platinum which serves as the anode, and filled with mercury, and the platinum wire of the negative pole dipped into the mercury,—an amalgam of barium, strontium, calcium, or magnesium is obtained. (H. Davy.) The assertion of Trommsdorff (*Gilb.* 30, 330), that by means of a battery of forty pairs of plates, each eight inches square, metal may be separated from hydrate of baryta, strontia, or lime, without the intervention of mercury, appears doubtful, inasmuch as this effect was not obtained either by Davy, Gay-Lussac & Thénard, or Jacquin, with their much more powerful batteries.

On introducing a solution of potash, baryta, or strontia, into the

apparatus described on page 451, only one-fourth of an atom of alkali is carried over to the negative cell for every atom of water decomposed. (Daniell.) Iron, acting as anode in aqueous solution of potash does not oxidate, but liberates all the oxygen as gas, even when it is immersed before the cathode. (Schönbein.) Many kinds of cast iron, however, although part of the oxygen is evolved on them as gases, dissolve in the form of ferrate of potash. (Poggendorff.)

Heavy Metallic Oxides.

Fused *Protoxide of Lead* is resolved into lead at the cathode and oxygen at the anode. Fused *Oxide of Antimony* is at first easily decomposed, yielding antimony at the cathode; but the oxygen separated at the anode converts the oxide of antimony there situated into infusible antimonic acid, which forms an insulating envelope round the anode, and gradually stops the current. (Faraday.)

Oxygen-salts of the Alkalis and Earths.

An electric current decomposes an atom of an oxygen-salt in the same time as it decomposes an atom of water or chloride of lead. If, for example, solution of sulphate of soda be introduced into the apparatus described on page 451, in which it is separated by two membranous diaphragms into three divisions, into the two outermost of which the platinum electrodes of a Daniell's constant battery are made to dip, and the quantities of gas determined which are evolved at the electrodes and in an interposed voltameter—the soda separated in the negative division, and the sulphuric acid set free in the positive division, being also estimated, —it is found that the volume of detonating gas collected in the voltameter is equal to the volume of hydrogen obtained in the negative division, together with that of the oxygen evolved in the positive division,—and that for every 9 parts (one atom) of water decomposed in the voltameter, 32 parts (one atom) of soda are set free in the negative, and 40 parts (one atom) of sulphuric acid in the positive division. (Similar results are obtained with sulphate of ammonia, sulphate of potash, phosphate of soda, carbonate of potash or soda, and nitrate of potash, excepting that in the last case ammonia is likewise formed.) If, instead of a voltameter, a tube containing fused chloride of lead be introduced into the circuit, the cathode being formed of a platinum wire, fused into the bottom of the tube, whilst a piece of graphite dips into the upper part to form the anode,—an atom of lead is deposited on the platinum for every atom of sulphate of soda (sal-ammoniac or common salt) decomposed. These experiments are favourable to the supposition that the oxygen-salts should be regarded as compounds of metals with so-called salt-radicals,—*e.g.*, sulphate of soda not as $Na\,O, SO^3$, but as $Na\,S\,O^4$—and that the same quantity of electricity which serves to separate an atom of oxygen, chlorine, or iodine, from an atom of hydrogen, or a metal, is likewise exactly sufficient to separate an atom of $S\,O^4$, or any other compound salt-radical from an atom of metal. (Daniell.)—Matteucci (*Ann. Chim. Phys.* 74, 99) obtained the same results by subjecting other salts to similar treatment. For every atom of water decomposed in the voltameter, he obtained from the saline solution 1 atom of hydrogen gas, 1 atom of oxygen, 1 atom of base, and 1 atom of acid.—Such was the case with sulphate of magnesia, excepting that there was a deficiency of $\frac{1}{10}$ in the magnesia separated,—with benzoate of potash, in which case the separated acid, being but

slightly soluble, could be directly weighed;—with benzoate of lime, in which case the lime also could be weighed;—and with benzoate of zinc, in the case of which, the benzoic acid and the metallic zinc were weighed, and no evolution of hydrogen gas took place.

[The theory which regards sulphate of soda as $Na\,S\,O^4$ certainly affords the simplest explanation of its electrolysis. Since, however, many weighty reasons may be urged against the adoption of this hypothesis, the following explanation may for the present be admitted. Sulphate of soda is $Na\,O, S\,O^3$; decomposition by the electric current is exerted only on the soda (since, by Faraday's law, $S\,O^3$ is incapable of direct decomposition). Sodium separates at the negative pole, where it decomposes water and yields soda and hydrogen gas. The oxygen which was combined with the sodium is transferred, together with the sulphuric acid, to the adjacent atom of sodium. An atom of oxygen is set free at the positive pole; and since the sodium which was combined with it goes towards the negative pole, the sulphuric acid is set free by secondary action,—or rather it passes from its state of combination with soda into that of combination with water. In the case of sulphate of copper, &c., similar actions take place, excepting that the metal liberated by the current does not decompose water. The decomposition of oxygen-salts of ammonia is most satisfactorily explained by adopting the ammonium theory of Berzelius, according to which, sulphate of ammonia, for example, which always contains water, is to be regarded as sulphate of oxide of ammonium ($N\,H^4\,O, S\,O^3$). The electric current decomposes the oxide of ammonium, just as it does a metallic oxide, into oxygen and ammonium, and the latter is resolved into hydrogen gas which escapes, and ammonia which remains in solution.—According to this view, the direct action of the electric current is confined to the decomposition of metallic oxides, and the transference of the acid from the decomposing oxide to the water is merely a consequence of this action. (Hess's Observations on Daniell's Theory—*vid. Pogg. 53, 505.*)].

When two salts, which do not precipitate each other, are dissolved together in water, their acids are simultaneously transferred to the positive, and their bases to the negative pole. (H. Davy.)

Iron acting as anode in aqueous solutions of oxygen-salts, evolves oxygen gas, just as platinum does, without oxidating—even when it is immersed in the liquid before the rest of the circuit is closed. (Schönbein.)

A moistened cup of *Carbonate of Ammonia*, filled with mercury, yields ammoniacal amalgam, just as sal-ammoniac does (p. 456). (Seebeck, *N. Gehl.* 5, 482, H. Davy.)

Fused *Borax* ($Na\,O, 2\,B\,O^3$) yields oxygen gas at the anode and boron at the cathode. Now, since fused boracic acid is not decomposible by the electric current, the separation of the boron must be attributed to indirect action; the current resolves the soda into oxygen and sodium—and the latter separates boron from the boracic acid. (Faraday.)—Fused *Quadroborate of Soda* ($Na\,O, 4\,B\,O^3$) conducts and shows signs of decomposition, but evolves gas at both poles: it therefore contains water. (Faraday.) Fused *Borate of Lead* is easily decomposed, yielding oxygen gas and metallic lead. (Faraday.)

The electric current resolves ordinary *Phosphate of Soda* in a state of solution into soda and phosphoric acid. (Davy.) Fused *Acid Phosphate of Soda* ($Na\,O, P\,O^5$) conducts and is decomposed; hydrogen gas, however, appears at the cathode, showing that water is present. (Faraday).—

Aqueous solution of *Borate* or *Phosphate of Ammonia* yields, when iron wires are used, less oxygen gas at the positive pole than is required to saturate the hydrogen evolved at the negative pole; and the positive wire becomes coated with white borate or phosphate of protoxide of iron. (Hisinger & Berzelius.)

Sulphate of Ammonia, Potash, or Soda, dissolved in water, is decomposed by the current—acid and oxygen appearing at the anode, alkali and hydrogen at the cathode. (H. Davy.)

Aqueous solution of *Sulphate of Ammonia,* in which iron wires are used as the poles, gives hydrogen gas and free ammonia at the negative pole; at the positive pole it yields oxygen gas—which is not evolved till the experiment has gone on for some time—and persulphate of iron. (Hisinger & Berzelius.)—Aqueous solution of *Neutral Sulphate of Potash* yields, with gold wires, an acid liquid in the positive, and an alkaline liquid in the negative side of the U-tube; these when mixed together produce a perfectly neutral solution.—When lead wires are employed, an insufficient quantity of oxygen gas is evolved, because a quantity of peroxide of lead is produced. When iron wires are used, the quantity of oxygen set free is likewise deficient, and, instead of it, a solution of protosulphate of iron is formed.—When the positive wire consists of zinc, no oxygen gas is evolved upon it; but it dissolves and forms sulphate of zinc, which, where it comes in contact with the negative alkaline liquid, deposits a layer of oxide of zinc. (Hisinger & Berzelius.)

Bisulphate of Potash ($K O, S O^3 + H O, S O^3$) is decomposible. (Faraday.) When the solution of this salt is decomposed in the apparatus described (p. 451), there is obtained for every 9 parts (1 atom) of water decomposed 18 parts ($\frac{1}{2}$ atom) more of sulphuric acid, and 9·9 parts ($\frac{1}{2}$ atom) less of potash; and in the negative cell, 19 parts less of sulphuric acid and 9·9 parts more of potash. In this case, the action of the current divides itself between $K O, S O^3$ on the one hand, and $H O, S O^3$ on the other. (Daniell.)

On filling two cups of *Heavy Spar* (sulphate of baryta) with water, connecting them by fibres of asbestus, and dipping into each of them one of the polar wires of a battery of 150 pairs of plates, a distinct trace of sulphuric acid is found after four days in the positive cup, and of baryta-water, together with carbonate of baryta in the negative cup.—With cups of *Cœlestin* (sulphate of strontia), the decomposition takes place more quickly, and with cups of *Gypsum* still more quickly. (H. Davy.) [The decomposibility of these bodies increases, therefore, in the same order as their solubility.]

When moistened *Sulphate of Magnesia* is formed into a cup, and the cup, with mercury in it, arranged in the manner described on page 458, amalgam of magnesium is obtained more readily than from moistened magnesia. (H. Davy.)

The electric current decomposes *Alum* dissolved in water. (H. Davy.)

Nitrate of Ammonia, in the fused state, yields hydrogen gas mixed with a little nitrogen at the cathode. In the state of solution, it yields oxygen gas at the anode, and hydrogen at the cathode, the latter sometimes mixed with a small quantity of nitrogen. (Faraday.) In aqueous solution of nitrate of ammonia, the positive iron wire evolves oxygen gas, becomes oxidized, and likewise dissolves; the negative wire evolves no gas and ammonia accumulates around it. (Hisinger & Berzelius.)

Nitrate of Potash dissolved in water conducts very well, yielding sometimes the normal quantity of hydrogen, sometimes less: sometimes,

again, secondary products are formed (Faraday); for ammonia is formed at the cathode (Daniell).—When iron wires are used, only the positive wire yields gas, viz., oxygen, but it likewise dissolves. The liquid at the negative wire likewise contains free ammonia, together with free potash. Zinc wires behave in the same manner, excepting that neither of them yields any gas, save a very small quantity, which appears on the negative wire every time the circuit is closed. (Hisinger & Berzelius.)

Nitrate of Baryta dissolved in water is resolved into acid and base. (H. Davy.)

Fused *Bottle Glass* is not decomposed; glass containing lead, slightly. (Faraday.)

If two cups be formed of any of the following *Siliceous Minerals*, filled with water—connected by asbestus—and subjected to the action of a powerful battery—their soluble constituents collect in the two cups. *Zeolite*, which contains 0·7 per cent. of soda, gives in two minutes distinct indications of soda and lime in the negative cup. *Lepidolite* gives potash. *Basalt* gives soda and potash in the negative cup, chlorine in the positive cup. Vitrified *Lava* from Ætna yields potash, soda, and lime in the negative cup. (H. Davy.)

Arseniate of Potash dissolved in water is slowly decomposed with separation of arsenic at the negative pole. (Bischof.)

Solid *Soap* (stearate of soda) stops the electric current after a few seconds,—because stearic acid, which is a non-conductor, separates at the anode. Touching the soap after this removes only the electricity of the negative pole. Hence we have an explanation of the *Negative Unipolarity** of soap observed by Erman. When the soap is wetted in the neighbourhood of the anode, the current is not impeded,—no unipolarity is observed. (Ohm, *Schw.* 59, 385.)

The *physiological effects* which accompany the passage of electricity through living animal bodies may be produced in either of the following ways. 1. The electricity may be actually transmitted through the solid parts of the body, and thus may directly affect the nerves. 2. It may decompose the salts contained in the liquids of the body, evolving oxygen and acid at the positive, hydrogen and alkali at the negative pole, as pointed out by Matteucci (*Schw.* 60, 305),—and bringing about a transpo-

* In addition to *Perfect Conductors* and *Non-conductors*, Erman distinguished the following classes of conductors: 1. *Bipolar Conductors* (water). Water, when connected with one pole of the battery and with the ground, conducts away the electricity of that pole. When connected with both poles, it does not allow the electricities accumulated in the poles to unite; but the poles retain their former tension, and this tension is likewise exhibited in the water, so that the half of the liquid next to the positive pole appears positive, the other half negative. [The great resistance which pure water opposes to the transposition of atoms enables the electric fluids to accumulate in the poles till they attain a very high tension; but they are by no means completely insulated, —electricity is continually passing into the water.]—2. *Unipolar Conductors*. Bodies of this class, like bipolar conductors, discharge each individual pole when they are connected with it and with the ground, and are likewise incapable, when placed between the poles, of bringing about the combination of the two electric fluids. But if when thus made to connect the poles, they are at the same time touched by a good conductor communicating with the ground, this conductor removes the electricity of one pole only, while that of the other remains undiminished. *Positive Unipolar Conductors* (the flame of alcohol and and other compounds containing carbon and hydrogen) are therefore such as when placed in the voltaic circuit communicate positive electricity to a good conductor;—*Negative Unipolar Conductors* (solid alkaline soap, dried white of egg,) on the contrary, communicate negative electricity under the same circumstances. [The cause of this peculiar property in soap has been explained above; similar causes are probably at work also in other substances in which the same peculiarity has been observed.]

sition of atoms in the liquids of the body situated between the electrodes; and since in particular organs, salts may be thus produced different from those previously existing, the result of the action may be irritation. The first of these modes of action is most conspicuous in electricity of great intensity, like that of the machine,—the second in galvanic electricity: and hence, perhaps, partly arises the difference between the sensations produced by these two kinds of electricity. Even a single pair of metallic plates connected with each other, and with different parts of the body, must produce transposition of atoms and change of composition—and this is the principal cause of the phenomena observed by Galvani and Humboldt.

Oxygen-Salts of Heavy Metallic Oxides.

The compounds of oxygen-acids with heavy metallic oxides usually give acid and oxygen gas at the anode, and reduced metal at the cathode,—no evolution of hydrogen taking place, excepting when the electric current is too strong, and its action is partly exerted on the water. In the case of some metallic salts (those of manganese, lead, and silver), the oxygen liberated at the positive pole combines with the metallic oxide there situated, and forms with it a peroxide which is precipitated. If the electrodes are formed of the same metal as that contained in the solution, the acid and oxygen which collect at the anode recover by dissolving it the metal which they have lost, and reproduce the original salt; thus the liquid remains unaltered, and the anode merely loses a quantity of metal equal to that which is reduced at the cathode.

Salts of Manganese deposit peroxide at the positive pole. (Balard.)

Sulphate of Zinc dissolved in water yields zinc at the negative pole, in the form of a powder possessing the metallic lustre.

Fused *Borate of Lead* yields lead at the cathode, oxygen and boracic acid at the anode. (H. Davy.)

Aqueous solution of *Nitrate* or *Acetate of Lead* yields lead at the negative pole, and brown peroxide of lead at the positive pole. (Faraday.)—If a voltameter be introduced into the circuit, it is found that the volume of oxygen gas evolved at the anode from solution of acetate of lead amounts to only $\frac{1}{10}$ of the detonating gas collected in the voltameter,—because the greater part of the oxygen is expended in forming the peroxide of lead, the quantity of which is to that of the lead separated at the cathode as 5 : 3 [?].—When the current is passed through acetate of lead which has been dehydrated and then fused, peroxide of lead is likewise produced at the anode, accompanied by a slight evolution of oxygen: for every 9 parts (1 atom) of water decomposed in the voltameter there is obtained at the cathode 103·4 parts (1 atom) of lead, and the weight of this lead is to that of the peroxide produced as 3 : 5 [?] (Matteucci, *Ann. Chim. Phys.* 71, 90.)

From a solution of *Protosulphate of Iron*, acted upon by a battery of 100 pairs, metallic iron is deposited in small granules on the *positive* platinum wire. (Becquerel.)

In solution of *Sulphate of Copper*, the negative platinum wire becomes covered with copper, while acid collects and oxygen gas is evolved at the positive wire. When copper wires are used, the positive wire loses as much metal as the negative wire gains, and the solution retains its original composition.

When active iron forms the anode in solution of sulphate of copper, it

dissolves without any copper being deposited on it;—but when the circuit is broken, the deposition takes place immediately. A passive iron wire acting as anode, and made to complete the circuit by its immersion, neither attracts copper nor dissolves, but evolves oxygen gas. (Schönbein.)

Solution of *Nitrate of Silver* deposits silver on the negative platinum wire, and crystallized peroxide of silver on the positive wire. (Ritter, Ruhland, *Schw.* 15, 414.)—In fused nitrate of silver, the anode evolves a large quantity of oxygen gas, while the cathode becomes covered with one atom of silver for every atom of water decomposed in the voltameter. The aqueous solution behaves in the same manner, evolving oxygen at the anode; but it likewise deposits peroxide. (Matteucci.)—Iron wire acting as anode does not oxidize, but liberates oxygen gas,—and when the current is strong, becomes covered with peroxide of silver. (Poggendorff, *Pogg.* 54, 357.)—Similarly, passive iron acting as anode becomes coated with peroxide of silver. (Schönbein.)

Nobili's Rings. When one of the electrodes consists of a plate of polished metal, the other of a fine platinum wire, the extremity of which approaches the plate within about half a line, there is often produced on that part of the plate which is immediately under the wire, a coloured ring or point surrounded with several, often four, concentric coloured rings. Thus a silver plate forming the anode produces coloured rings in solutions of phosphoric acid, carbonate of potash, sulphate of soda, sal-ammoniac, chloride of potassium or sodium (in which metallic chlorides, rings are likewise formed on copper and brass, but not on zinc or platinum), tartar emetic, sulphate of zinc, chloride of cobalt, sulphate, nitrate or acetate of copper, chloride of platinum, &c. Solutions of sulphate of manganese, nitrate of bismuth, and acetate of lead, likewise form negative rings on plates of gold or platinum. A silver plate likewise has rings formed upon it when it serves as the cathode in solutions of tartar emetic, salts of copper, or chloride of platinum. (Nobili.)

[These phenomena belong to the theory of Newton's Coloured Rings,—and, according to Faraday, Warington, and Schönbein, arise from products of decomposition deposited on the metallic plate in films of various thickness. These products of decomposition are sometimes formed only from the liquid; thus, salts of manganese deposit peroxide of manganese, —salts of lead peroxide of lead,—and salts of bismuth probably deposit peroxide of bismuth; and these deposits form coloured rings on plates of gold and platinum.—Sometimes the deposits arise from the combination of a substance separated from the liquid with the metal of the plate; thus, metallic chlorides form on silver or copper insoluble chloride of silver or dichloride of copper; and the oxygen acids or their salts probably form peroxide of silver on silver plates.—When the silver acts as cathode, the rings are formed by films of the precipitated metal of different degrees of thickness.]

The rings produced by acetate of lead exhibit, on chemical analysis, the reactions of peroxide of lead. Iodine in a state of sublimation produces the same colours on plates of silver or copper; they are likewise exhibited by any metal which when heated in the air becomes covered with a coat of oxide continually increasing in thickness. (Warington, *Phil. Mag. J.* 16, 52.)

The more oxidable metals, when used as anodes in nitrate or acetate of lead, do not allow of the formation of peroxide of lead; iron alone forms an exception, because it soon passes into the passive state: an iron

wire under these circumstances quickly and repeatedly becomes red, blue, yellow, red, blue, yellow, &c. The colour, however, becomes deeper every time, and at last so deep that the different tints cannot be distinguished. (Schönbein.)

To form a Nobili's monochromatic deposit on platinum, the following solutions may be used; Chloride of manganese in 8 parts of water, sulphate of manganese and potash in 12, acetate of manganese in 15, succinate of manganese in 16, or hippurate of manganese in 12 parts of water. A well-polished platinum capsule is filled with one of these solutions, and connected with the positive pole of a battery of 4 pairs of plates (each plate 36 square inches in surface), immersed in dilute sulphuric acid (if a stronger battery is used the solution of the salt must be more dilute); a disk of platinum $\frac{3}{4}$ of an inch in diameter is then dipped horizontally into the liquid to form the cathode. With sulphate of manganese and potash, or with succinate or acetate of manganese, one uniform tint is invariably produced, first golden yellow, then purple, then green; the current must therefore be stopped as soon as the desired tint is completely developed. With hippurate of manganese the capsule is first tinted golden yellow, then of a splendid bluish purple red. Chloride of manganese yields very beautiful broad alternating rings of purple green, golden yellow, and blue, surrounded by a broad belt of golden yellow. (R. Böttger, *Pogg.* 50, 45.)

Nobili's rings may also be formed by a simple galvanic circuit. When a plate of silver immersed in a solution of sulphate of copper is touched with the pointed extremity of a piece of zinc, there are formed round the point of contact a number of blue and green rings, which, when the zinc is removed, run through several changes of colour, finally becoming dark blue and lightish green.—In the colourless copper solution formed by leaving copper filings in contact with a saturated solution of sal-ammoniac in a closed vessel containing air,—silver or platinum becomes covered with copper, if it be touched below the surface of the liquid with a pointed piece of zinc;—but when the zinc is removed, the coating of copper gradually disappears, the action commencing from the outside (where the coating is thinnest) and proceeding towards the middle. (Fechner, *Schw.* 55, 442.) If however the platinum thus covered with copper be immediately dipped into water, so as to remove the ammoniacal liquid by which it would be redissolved, the coppering remains permanent; and if the zinc be left for a longer time, about two minutes, in contact with the platinum in the ammoniacal solution of copper, until it evolves gas and precipitates copper of a black colour, the platinum loses its thin coating of copper and becomes tinted with various shades of yellow, green, red, and especially black, which latter colour it then retains after drying. (R. Böttger, *J. pr. Chem.* 8, 476.)

(For the decomposition of organic compounds by the electric current, *vid.* Oxalic acid, Tartaric acid, Acetic acid, Wood-spirit, Alcohol, Ether, and the Organic Bases.)

Decomposition of several Liquids in Contact with one another.

When the electric current has to traverse a number of liquids [or to effect a transportation of atoms in them] which are either in immediate contact or separated from one another by a porous body, it at first deposits

at the anode the anions of that liquid only which is in contact with the anode; but after the current has acted for a longer time, the anions of the liquid situated at the negative pole, or in the middle, are likewise transferred to the anode. Similar effects are produced at the cathode.

[At the surface of contact of the different liquids, an atom of anion of the liquid situated next to the cathode is transferred by atomic transposition to an atom of cation of the liquid lying next to the anode, and thus the anion-atoms of the former liquid continually advance nearer and nearer to the anode, and the cation-atoms of the latter to the cathode; but they are not liberated till they actually reach the electrodes. If, for example, water is situated at the positive, and hydrochloric acid at the negative pole, an atom of water is decomposed at the former with separation of oxygen, and an atom of hydrochloric acid at the latter with separation of hydrogen. By atomic transposition, an atom of hydrogen from the water, and an atom of chlorine from the hydrochloric acid, arrive at the surface of separation, and there combine to form hydrochloric acid. (*App.* 33.) The first atom of chlorine which passes the boundary is followed by a second, and so on; and thus, at last, the compound of chlorine and hydrogen arrives at the positive pole—and not till then is the chlorine set free at that pole. If sulphate of copper be placed at the negative, and water at the positive pole, copper is set free at the former and oxygen at the latter; while at the boundary, the oxygen of the oxide of copper combines with the hydrogen of the water, which at the same time takes up the sulphuric acid previously liberated.—If chloride of sodium is situated at the negative, and sulphate of copper at the positive pole, sodium is separated at the former (but by contact with the water it forms soda and liberates hydrogen)—oxygen gas and sulphuric acid at the positive pole: chlorine and copper combine at the border.]

For making experiments relating to this matter, the following apparatus may be used: *App.* 2, in which the two dishes, cups, or tubes, *a*, *b*, are connected by moistened fibres of asbestus, and have the polar wires immersed in them;—*App.* 3, with a diaphragm of bladder;—the U-tube, *App.* 4, which either contains one liquid in each arm (sometimes the two being in immediate contact, sometimes separated at *h* by clay, cotton, &c.), or a heavier liquid at *h*, and a separate liquid in each arm;—*App.* 5, to which similar remarks apply;—*App.* 6, in which the liquids are simply laid one upon the other;—*App.* 7, in which the tube *a* is closed at bottom by a piece of bladder or clay;—*App.* 8, in which also the tubes *a b* are stopped with clay;—*App.* 9, of which the same may be said as of *App.* 2.—In the delineations of all these arrangements, a galvanic battery must be supposed to be introduced in place of the galvanometer.

Two Liquids in two Divisions.

When water is separated from sulphuric acid by a membrane, the current is less obstructed if the positive electricity be conducted into the water, and the negative into the acid, than in the contrary case. (Matteucci.)

The following table exhibits a general view of the decompositions observed. The first column shows the apparatus in which the experiment was made; the second, third, and fourth, the liquids placed in the positive and negative divisions respectively; the fifth, sixth, and seventh columns show what substances were separated at the positive and negative polar wires, which usually consisted of platinum;—in the last column the name

of the observer is given.—*c* denotes the middle vessel occurring in several arrangements, and the liquid contained in it.

App.	Liquids in +	in c	in −	Substances separated at +	in c	at −	Observer.
2	HO . .	. .	HO, SO^3	O . .	.	S . .	H. Davy [1]
2	HO . .	. .	HCl . .	O . .	.	H . .	Connell [2]
2	HO . .	. .	HI . .	O . .	.	H . .	——
2	HCl . .	. .	HO . .	Cl . .	.	H . .	——
2	HI . .	. .	HO . .	I . .	.	H . .	——
2	HO . .	. .	KCl . .	O . .	.	KO; H	—— [3]
2	HO . .	. .	KI . .	O . .	.	KO; H	—— [3]
2	KCl . .	. .	HO . .	Cl . .	.	H . .	——
2	KI . .	. .	HO . .	I . .	.	H . .	——
2	HO . .	. .	KO, SO^3	SO^3; O	.	KO; H	H. Davy [4]
2	KO, SO^3	. .	HO . .	— —	.	— —	—— [4]
2	HO . .	. .	CaO, SO^3	— —	.	CaO; H	—— [5]
2	CaO, SO^3	. .	HO . .	— —	.	— —	—— [5]
4	CaO, NO^5	. .	HO . .	NO^5, O	.	— —	—— [6]
9	MgO, SO^3	HO .	HO . .	SO^3, O	MgO	H . .	—— [7]
8	KO . .	HO .	HO . .	O . .	.	KO; H	Becquerel
	$CaCl$ . .	. .	HO . .	Cl . .	.	CaO; H	His. & Berz. [8]
	HO . .	. .	$CaCl$.	— . .	.	— —	—— [8]
8	CuO, SO^3	HO .	HO . .	SO^3; O	.	H . .	Becquerel [9]
8	KO, NO^5	KO, NO^5	CuO, SO^3	NO^5; O	.	Cu .	—— [10]
4	CuO, NO^5	. .	NH^4, Cl	NO^5; O	.	NH^3H	Gm. [11]
7	CuO, SO^3	. .	KO . .	SO^3; O	.	H . .	Daniell [12]
8	$NaCl$ . .	$NaCl$.	$MgCl$.	Cl . .	.	Mg .	Becquerel [13]
8	— . .	. .	GCl . .	Cl . .	.	G . .	—— [14]
8	— . .	. .	$ZrCl$ . .	Cl . .	.	Zr . .	——
8	— . .	. .	$FeCl$ . .	Cl . .	.	Fe . .	——
4	NH^4, Cl .	. .	NaO, SO^3	Cl, SO^3	.	NaO .	Gm. [15]

1. The hydrogen directly separated at the negative pole from the water of the oil of vitriol combines, according to Faraday's view, with the oxygen of the sulphuric acid, and precipitates of sulphur.

2. At first, hydrochloric or hydriodic acid collects in the positive division, free chlorine or iodine showing itself only when the current has continued for a very long time. Hence the hydrogen-acids do not appear to be directly decomposed. (Connell.) [This is a conclusion which, according to what has been already observed (p. 456), we are not obliged to admit.]

3. In these cases, also, hydrochloric or hydriodic acid collects in the positive cup, but no free chlorine or iodine. (Connell.)

4. When the current has been continued for a certain time, all the potash is found in the negative, and all the acid in the positive cup. Other salts of the alkalis likewise behave with water in the same manner as sulphate of potash. If, therefore, the positive cup contains water coloured with litmus, and the negative cup water coloured with turmeric, both liquids become reddened, because acid is transferred to the positive and alkali to the negative pole, from the salts contained in these colouring matters. The greater the length of the asbestus fibres, or the distance between the positive and negative wire, the more slowly does the transference of acid and alkali take place. Thus, with a battery of 100 pairs, only five minutes elapse before the appearance of acid in the positive cup, when the distance between the polar wires is only an inch; but fourteen hours are required when the distance amounts to 8 inches,—the positive

and the middle cup *c*, as well as the two bundles of asbestus (*App.* 9), containing water.—If water coloured blue by litmus is contained in the positive and middle cups, and sulphate of potash in the negative cup, the first reddening takes place at the positive wire, and not in the middle cup or the two bundles of asbestus—although the sulphuric acid eliminated from the negative cup is obliged to pass along the asbestus fibres and through the middle cup, before it reaches the positive wire. Similarly, if the positive cup contains sulphate of potash, and the middle and negative cups water coloured yellow by turmeric, the first reddening produced by the liberated potash appears at the negative wire. (H. Davy.)—If the positive arm and the lower part of the negative arm of the U-tube (*App.* 4) be filled with solution of sulphate of potash, the portion of the solution which occupies the negative arm carefully covered with a layer of water, the water with washed cotton, the cotton with a second layer of water, and the negative wire of a small 50-pair battery immersed in the latter, —potash appears in the upper layer of water. If the two layers of water are coloured with tincture of the flower of *Alcea rosea*, the negative wire dipped into the solution of sulphate of potash, and the positive wire into the uppermost layer of water, reddening at first takes place close to the positive wire,—and not till the upper layer of water is completely reddened does any red colour appear in the lower. (Gm.)

5. In these two experiments, either the positive or the negative cup was made of gypsum and filled with water; the gypsum was gradually dissolved by the water and decomposed. (H. Davy.)

6. The positive arm of the U-tube and the lowest part of the negative arm contained a concentrated solution of nitrate of lime; on this was carefully placed—first water, then wet cotton, then again water. The negative wire of a small fifty-pair battery was then immersed in the upper layer of water for forty-eight hours. Both the upper and lower layers of water were then found to contain lime; a small portion of lime was deposited on the negative wire, but the greater portion in the form of crystallized hydrate, at the boundary between the nitrate of lime and the water. When three layers of water are placed in the negative arm, separated by two layers of cotton, and the two upper layers coloured with turmeric, reddening at first takes place in the upper layer close to the negative wire; and not till the upper layer is completely reddened does any tinge of red colour appear in the lower, the reddening then proceeding from the upper to the lower part of the layer. Similar remarks apply to the green colouring which takes place when the two layers of water are coloured with tincture of the flowers of *Alcea rosea*. (Gm.)

7. In this experiment, magnesia was precipitated in the middle cup, but did not reach the negative wire. (H. Davy.) Faraday also found that when water perfectly free from alkali is placed under a solution of sulphate of magnesia, the negative wire dipping into the former and the positive into the latter, the magnesia is deposited, not upon the negative wire, but at the surface of separation between the two liquids. I have obtained the same result with *App.* 4; the whole of the magnesia was deposited at the boundary between the two liquids, none at the negative wire. [The sulphate of magnesia is resolved into sulphuric acid and oxygen, which travel towards the positive pole, and magnesium which goes towards the negative pole. Arrived at the boundary of the two liquids, the magnesium combines with the oxygen of the nearest atom of water, and forms magnesia, which being but very slightly soluble in

water, is precipitated.] So likewise it was found by Sir H. Davy that when the positive cup (*App.* 2) contains nitrate of silver, and the negative cup water, metallic silver is deposited along the whole length of the asbestus fibres.

8. Hisinger & Berzelius employed in their experiments the U-tube, the open ends of which were turned downwards and closed with stoppers through which the polar wires passed; the bend of the tube had an opening for the purpose of collecting the gas which arose. But this evolution of gas must have caused the liquids to mix.

9. No copper reaches the negative wire, because it is not soluble in water. (Becquerel.)

10. At the beginning, crystals of sulphate of copper and potash are deposited in the negative tube, because potash gets into it: these, however, are destroyed as soon as the nitrate of potash is completely decomposed, and then sulphuric acid collects in the positive tube. (Becquerel.)

11. The heavier copper solution likewise filled a portion of the negative arm; after twenty-four hours action of a twelve-pair battery, not a trace of chlorine was found in the liquid of the positive arm, and but a slight tinge of copper at the negative wire. (Gm.)

12. On the lower surface of the bladder which closes the negative tube containing potash, a deposit of metallic copper is formed, mixed with black oxide and blue hydrated oxide, the latter possibly arising from the ordinary chemical action of the potash on the copper-salt. Similar relations are likewise exhibited by nitrate of lead, subnitrate of mercury, and nitrate of silver, and by the protosulphates of iron and palladium. Sulphate of magnesia, on the other hand, merely deposits magnesia on the bladder. (Daniell.)

13. In this and the following experiments of Becquerel, the solutions must be very concentrated, otherwise nothing but water will be decomposed; the battery must also contain from thirty to one hundred pairs of plates. Not a trace of hydrogen is evolved. (Becquerel.)

14. The solution of chloride of glucinum, and that of chloride of zirconium must be mixed with a small quantity of chloride of iron,—otherwise no glucinum or zirconium will be separated. The first portions of these metals deposited on the negative wire contain iron,—the subsequent portions are pure. (Becquerel.)

15. Sulphuric acid always collected in the positive arm, but the occurrence of ammonia in the negative arm was not constant. When the positive arm and the lower part of the negative arm of the U-tube contain nitrate of lead,—the solution in the negative arm being covered with a layer of cotton an inch high, moistened with solution of nitre, and a portion of the same solution being placed above the cotton,—a large quantity of peroxide of lead is deposited on the positive wire after twenty-four hours action of a small fifty-pair battery, but no lead on the negative wire. (Gm.)

Two Liquids in three Divisions, one Liquid in the middle, and the other in the two exterior Divisions.

All the experiments of Davy and Connell, enumerated in the following table, were made with *App.* 9; De la Rive, on the other hand, formed his three divisions by means of two upright sheets of bladder.

Liquids.		Substances separated.		
in the + and − cups.	in the middle cup.	at +	at −	Observer.
H O	I or Br	O	H	Connell [1]
H O	SO^3 dilute	SO^3; O	H	—— [2]
H O	K O dilute	O	K O; H	—— [2]
H O	K Cl	H Cl, O	K O; H	H. Davy [3]
H O	NH^4 Cl	H Cl, O	NH^3; H	Connell
H O	K I	IO^5	K O; H	—— [4]
NH^4 Cl	Zn O, SO^3	Cl	NH^3, H	De la Rive [5]
Zn O, SO^3	NH^4 Cl	SO^3, O	Zn	—— [5]

1. Bromine or iodine dissolved in water does not pass over either into the positive or into the negative cup. (Connell.)

2. The passage of sulphuric acid into the positive, and that of potash into the negative cup, becomes evident in a few minutes. Not a trace of these substances passes into the opposite cup; consequently, the transit is caused, not by capillarity but by the electric current. It appears then that acids can travel to the positive pole without the assistance of bases, and alkalis to the negative pole without the help of acids. (Connell.)

3. Chloride of calcium and chloride of iron behave just like chloride of potassium. (Connell.)

4. Hydriodic acid is at first separated between the iodide of potassium and the positive water; but this acid is converted into iodic acid by the oxygen passing over to the positive pole. If therefore two cups filled with water be placed on the positive side, hydriodic acid will be found in the one which touches the iodide of potassium, and iodic acid in that in which the positive wire is immersed. (Connell.)

5. From these experiments it appears that those liquids only are decomposed which are in contact with the polar wires. [If the experiment had been continued for a longer time, it is probable that the elements of the middle liquid would likewise have appeared at the poles.]

When the two outer cups (*App.* 9) contain common salt, and the middle one nitrate of silver, chlorine immediately appears in the positive cup, and soda, together with hydrogen gas, in the negative cup. In the middle cup two precipitates are formed,—one of a flocculent character, where the soda from the positive cup enters the silver solution, the other of a thick consistence, where the chlorine from the negative side enters the same solution. (H. Davy.)

A laurel leaf with one end dipping into the water in cup *a* (*App.* 2), and the other end in *b*, becomes brown after the current has acted upon it for some time, looking as if it had been burnt; the water in the positive cup remains perfectly clear and smells like peach blossom; that in the negative cup is found to contain potash, lime, resin, and green colouring matter. A peppermint plant, after being exposed in this manner to the action of the current for ten minutes, recovers itself; but if the current be suffered to act upon it for four hours, it withers. At the same time, sulphuric acid, hydrochloric acid, and an acid which precipitates chloride of calcium (oxalic acid ?) collect in the positive cup,—potash and lime in the negative cup. (H. Davy.)

If the lower ends of two glass tubes be closed by the extremities of a shoot of *Cactus flagelliformis*, the tubes filled with water and a polar wire dipped into each, the end of the shoot which is turned towards the positive pole becomes yellowish and shrinks up, whilst the other end acquires a dark green colour and swells up. The water of the positive tube is found to contain chlorine, that in the negative tube potash. (Hisinger, *Gilb.* 27, 304.)

When a piece of bladder is used as a diaphragm in pure water, the common salt contained in it is decomposed, chlorine being eliminated at the positive and sodium at the negative pole. (H. Davy.) (Hence Pachiani's supposed generation of chlorine from water. *Gilb.* 21, 108, 113, and 125; 22, 202, 208, 210, and 220; 23, 463.)—A piece of muscle 2 inches long and $\frac{1}{2}$ an inch thick being laid with its ends dipping into two glasses filled with water, and subjected for five days to the action of the current of a 150-pair battery, becomes dry and hard and leaves no saline residue when burnt; but the positive cup is found to contain phosphoric, sulphuric, hydrochloric, and nitric acid, and the negative cup ammonia, potash, soda, and iron.—When a well-washed finger is dipped into the positive and another into the negative cup, phosphoric, sulphuric, and hydrochloric acid collect in the former, alkali in the latter. (H. Davy.)

If the lower ends of two glass tubes be stopped up by a piece of muscular flesh kept moist by immersion in water, the tubes filled with water, and an electric current passed into the water for twenty-four hours, the end of the piece of flesh in the positive tube appears like coagulated white of egg, being also transparent and destitute of smell; that in the negative tube is more strongly reddened, appears translucent, smells putrid, and is covered with a coating of lymph. The slightly coloured water of the positive tube contains hydrocholoric acid with flakes of coagulated albumen, the yellowish water of the negative tube contains soda. (Hisinger.)

Minerals likewise contain—probably from the sea-water which once covered them—certain salts, the constituents of which are transferred under similar circumstances to the polar wires. If a cup of Carrara marble be placed in a platinum crucible, water poured into both vessels till it reaches a little above the edge of the marble cup, the crucible connected with the positive pole, and the negative wire dipped into the water of the marble cup,—soda as well as lime collects in the latter. Clay slate and serpentine yield soda in a similar manner. Glass vessels also containing water through which the electric current is passed, are attacked and yield soda at the negative pole. (H. Davy.)

Three Liquids.

	Liquids.			Substances separated.			
App.	in +	in c	in −	at +	in c	at −	Observer.
9	H O	K O, SO^3	Ba Cl	SO^3, Cl H	. .	. .	H. Davy[1]
9	K O, SO^3	Ba Cl	H O	. .	. .	Ba O, K O	—— [2]
9	Ba Cl	K O, SO^3	H O	. .	Ba O, SO^3	K O	—— [3]
9	H O	Ag O, SO^3	Ba Cl	SO^3 .	Ag Cl	. .	—— [4]
9	H O	K O	K O, SO^3	SO^3 .	. .	. .	—— [5]
9	K O, SO^3	SO^3	H O	. .	. .	K O	—— [6]

1. Sulphuric acid begins to show itself in the water in five minutes, hydrochloric acid not till after two hours. (H. Davy.)

2. Baryta appears in the water after the lapse of some minutes, potash in an hour.

3. Potash instantly appears in the water, but no baryta passes over into that liquid even in ten hours, because in passing through the sulphate of potash in the middle vessel it is precipitated in the form of sulphate of baryta. (H. Davy.)

4. Hydrochloric acid could not pass over to the water, because it was precipitated in the middle vessel by the sulphate of silver. (H. Davy.)

5. Instead of potash, the middle vessel may contain ammonia, soda, or lime-water; the sulphuric acid will still go through. When the alkaline solutions are dilute, sulphuric acid shows itself in the water in five minutes (with a battery of 150 pairs); but through concentrated potash or soda it passes but slowly. Similar effects are produced when nitre or common salt is substituted for sulphate of potash. In the same manner, hydrochloric and nitric acids pass through baryta or strontian-water in the middle cup. But if the negative cup contains a soluble sulphate, *e. g.* sulphate of potash, and the middle one baryta-water, the whole of the sulphuric acid which passes into the latter is precipitated as sulphate of baryta, and no acid appears in the positive cup. When strontian-water is placed in the middle cup, a trace of sulphuric acid appears in the positive cup after three days [probably because sulphate of strontia is somewhat more soluble]. (H. Davy.)

6. Instead of sulphate of potash the positive cup may contain any other salt of potash, soda, lime, or magnesia, and the middle cup may be filled with hydrochloric or nitric acid instead of sulphuric; *e. g.* nitrate of lime and hydrochloric acid, sulphate of soda and hydrochloric acid, chloride of calcium and sulphuric acid, chloride of magnesium and sulphuric acid; similarly, salts of baryta or strontia with hydrochloric or nitric acid. The base always goes through the acid in the middle cup to the water in the negative cup; the stronger the acid in the middle cup, the slower is the passage; but with a battery of 150 pairs, decisive results are always obtained in less than forty-eight hours. If however the base should form an insoluble salt with the acid in the middle cup,—*e.g.* when a baryta or strontia salt is contained in the positive cup and sulphuric acid in the middle,—the base never reaches the negative cup.—If the positive cup contains proto-sulphate of iron, the middle hydrochloric acid, and the negative cup water, green hydrate of protoxide of iron appears after ten hours in the asbestus between the middle and negative cup, and in three days a large quantity of hydrate is deposited in the negative cup. Sulphate of copper, nitrate of lead, and chloride of zinc, behave in a similar manner. (H. Davy.)

The following experiments were made with a U-tube; the heaviest liquid filled the curved part, the two others the arms. The current of a ten-pair battery was passed through the apparatus for twenty-four hours. It follows from these experiments that, with currents of small tension, liquids do not transmit their constituents very quickly to the electrodes farthest removed from them. (Gm.)

Liquids.			There is found,	
in +	in the middle.	in −	in + liquid.	in − liquid.
NH^4Cl	Na Cl	Na O, SO^3	no SO^3	no NH^3
Na Cl	Ca Cl	NH^3, NO^5	no NO^5 (but ClO^5)	
NH^4Cl	H O, SO^3	2Na O, PO^5	no PO^5	no NH^3
Ca O, NO^5	Na O, NO^5	NH^4Cl	no Cl	no Ca O
Pb O, NO^5	K O, NO^5	NH^4Cl	Pb O^2, no Cl	no Pb on − wire
Cu O, NO^5	Ca O, NO^5	NH^4Cl	no Cl	no Cu on − wire
Ag O, NO^5	K O, NO^5	K O, SO^3	Ag O^2, no SO^3	no Ag on − wire

1. No copper or oxide of copper is deposited on any part of the apparatus. (Gm.)

If the positive cup (*App.* 2) contains nitrate of baryta, the negative cup sulphate of copper, and the asbestus *h* is saturated with solution of common salt, no turbidity is produced in the nitrate of baryta by the action of the current, because the sulphuric acid which is carried in the

direction of the positive pole remains (as sulphate of soda) in the solution of common salt. (Becquerel.)

These experiments are decidedly opposed to De la Rive's theory of of electrolysis. (p. 433.)

The tube *a* (*App.* 7) is closed at the bottom with clay saturated with acetate of soda, and contains acetate of iron with which is mixed a trace of acetate, sulphate, or nitrate of manganese; it is likewise immersed in the vessel *b* filled with nitrate of copper: under these circumstances, the current of a single pair of plates is sufficient to coat the positive platinum wire which dips into *a* (the negative wire dipping into *b*), with brown peroxide of manganese, and in a few hours to separate all the manganese from the iron solution. Sometimes the liquid in *a* acquires a transient rose colour towards the end of the action. A salt of lead (instead of manganese) mixed with the iron salt yields brown-black crystals of peroxide of lead on the positive wire, as long as any lead remains in the liquid; in this case, however, a battery of several pairs is required. (Becquerel.)

Electrical Polarization.—Secondary Charge.

When an electric current has passed for some time from two homogeneous (or even heterogeneous) metals into a liquid—if the metals be then separated from the electrical source and metallically connected (by means of a galvanometer) whilst they remain in contact with the liquid, —a current of electricity passes from the one to the other, through the metallic connection, in the direction opposite to that of the original current; that is to say, positive electricity passes from the former anode through the galvanometer to the cathode. This *secondary* current is often produced when the two pieces of metal, after being acted upon by the first or *primary* current, are placed in contact with fresh liquid instead of that in which they were previously immersed; likewise when the liquid which has been exposed to the action of the current is placed in contact with two fresh pieces of metal.

[The secondary current is for the most part referable to decompositions produced in the liquid by the primary current, and to the various products of decomposition partly deposited on the anode and cathode, partly collected in the positive and negative halves of the liquid. As soon as the primary current ceases, a chemical reaction of these products upon each other and upon the liquid commences, and thus an electric current is produced. This current always takes the direction opposite to that of the primary current, because the latter has accumulated electro-negative substances at the positive pole, and electro-positive substances at the negative pole.]

Two platinum wires conducting the electric current through mercury do not become polarized. (Schönbein; De la Rive.)

Platinum wires in water give a weaker secondary current than the same wires in dilute acids. (De la Rive.)

Electrodes of spongy platinum in water or dilute sulphuric acid give a much stronger and more permanent secondary current than electrodes of compact platinum. Platinum wire, the surface of which has been brought into the pulverulent state by alternating currents, behaves like spongy platinum. (De la Rive.)

Platinum acting as cathode is freed by hydrogen from all adhering

oxide, and thus brought into a state in which it may be slightly acted upon by water containing acids or air; platinum which has been used as an anode (and, in a less degree, that which has been exposed to the air) is coated with oxide. This chemical difference between the two pieces of platinum produces the secondary current.—If two platinum plates be equally well cleaned, but one dried in the open air and the other in vacuo over oil of vitriol, the former, which has become oxidized by exposure to the air will be negative towards the latter in dilute sulphuric or nitric acid, but positive in strong nitric acid—because this acid dissolves the oxide. (De la Rive.)

If a cell filled with dilute sulphuric acid is terminated at its two ends by a zinc and a platinum plate, and divided in the middle by a second platinum plate into an exciting and a decomposing cell—the zinc plate being connected with the first platinum plate, but in such a manner that a piece of paper moistened with solution of iodide of potassium may be introduced into the circuit,—decomposition of the iodide of potassium ensues, and the needle is slightly deflected. If the paper be then removed and the circuit metallically closed, the deflection is at first much stronger, but soon ceases in consequence of the polarization of the platinum plates. If the paper be then reintroduced, no more decomposition of the iodide of potassium ensues: it again takes place, however, if the circuit be left open for five or ten minutes. If the circuit has been metallically closed for an hour or two, a feeble current only is produced after it has been left open for ten minutes; and the two platinum plates connected by the galvanometer now produce a counter-current, whereby positive electricity passes from the first platinum plate to the second. (Faraday.)

In dilute hydrochloric acid, platinum, gold and silver give secondary currents; in dilute sulphuric acid, only platinum. This metal, both in pure oil of vitriol and in oil of vitriol diluted with two or three parts of water, produces a strong secondary current, even if the primary current be so feeble as scarcely to decompose iodide of potassium. The secondary current often continues for hours, gradually diminishing in power. The wires retain their polarization longer when separate than when united. When the secondary current has ceased, it may be again excited in the same direction by keeping the wires separate for a time, and will be more powerful the longer the separation has lasted,—but always feeble. A secondary current is likewise obtained when the negative platinum wire is removed and replaced by one which has not been used. (Schönbein.)

Copper electrodes exhibit the strongest polarization when they act upon a solution of common salt; then follows water, then dilute sulphuric acid, then dilute nitric acid. For when the current is made to act upon the water-cell till the polarization has attained its maximum, and the plates are then removed from the circuit and connected with the chloride of sodium cell and the galvanometer, the counter-current amounts to 14°; but when the chloride of sodium cell has been exposed to the current of the battery, the counter-current excited on connection with the water cell amounts to 17°. The polarized water cell connected with the sulphuric acid cell gives 11·2°; the polarized sulphuric acid cell, on the contrary, connected with the water cell, gives only 5°; and the polarized nitric acid cell, when connected with the water cell, gives only 0·5°. (Buff.)

The primary current polarizes both the electrodes and the liquid, sometimes the former in a greater degree, sometimes the latter. A secondary current is likewise excited when the two platinum wires, after

they have been acted upon by the primary current, are replaced by two unused wires connected together by the galvanometer. If the wire which has conducted positive electricity into dilute hydrochloric acid in the U-tube be made to dip into the negative arm, and the other wire into the positive arm, the direction of the current will be such as to show that the polarization of the hydrochloric acid is stronger than that of the wires. With sulphuric acid either concentrated or dilute, the action is at first exactly the reverse of that just described, positive electricity going from the wire which formed the anode through the galvanometer to the other wire; but this current gradually diminishes and is at last reversed, —a proof that the polarization of the sulphuric acid, though weaker, is more lasting than that of the wires.—The platinum wires through which the primary current has passed into dilute acid likewise give a secondary current when immersed in fresh dilute acid.—A current so feeble as no longer to cause evolution of gas, is still capable, even when the wires are replaced by fresh ones, of polarizing hydrochloric acid—which on the whole is susceptible of stronger polarization,—but not sulphuric acid, in the case of which at least a trace of gas must be evolved. With a stronger current, sulphuric acid retains its polarization, even after it has been heated to the boiling point in both arms of the U-tube, provided the portions of liquid in the two arms have been prevented from mixing. (Schönbein.)

A platinum wire which has formed the anode in water or dilute sulphuric acid, loses its polarization in hydrogen gas, because that gas removes the oxygen which surrounds the platinum, probably in the state of peroxide of hydrogen [or, according to De la Rive, of oxide of platinum]; and a wire which has conducted negative electricity (or served as cathode) loses its polarization in chlorine gas or bromine vapour, and more slowly in oxygen gas, those substances removing the hydrogen [or, according to De la Rive's view, forming a coating of chloride, bromide, or oxide of platinum]. Both wires lose their polarization by ignition, which removes both oxygen and hydrogen. (Schönbein.)

Wires and liquids may also be polarized by ordinary chemical means. Clean platinum wire placed in hydrogen gas becomes in a few seconds positive towards other platinum wires, because an envelope of hydrogen is formed around it [or, according to De la Rive's view, because it is entirely freed from oxide by the hydrogen]. Gold and silver are not polarized in hydrogen gas. In oxygen gas, neither platinum, gold, nor silver is polarized; but all three of these metals are polarized by chlorine gas or bromine vapour.—Similarly, dilute sulphuric acid which has been shaken up with hydrogen gas, is positive towards sulphuric acid not so treated; and water, after being agitated with hydrogen gas, is positive towards ordinary water, when the electrodes are formed of platinum, but not when they consist of gold or silver. Dilute sulphuric acid agitated with oxygen gas, gives no current with other sulphuric acid; but dilute sulphuric acid mixed with bromine or chlorine, is negative towards ordinary sulphuric acid with platinum electrodes, but not with electrodes of gold or silver. (Schönbein.)

A platinum plate which has served as positive pole in a watery liquid, absorbs hydrogen when immersed in that gas [which, according to De la Rive, combines with the oxygen of the oxide of platinum], and a plate which has formed the negative pole absorbs oxygen gas [according to De la Rive, because it again becomes coated with oxide]. Platinum, after immersion in oxygen gas, is negative in a watery liquid towards platinum which has been immersed in hydrogen gas. (Matteucci.)

Charcoal or porous coke, used as the negative pole in a watery liquid, liberates no hydrogen at first, but condenses it; hence these substances, when afterwards placed in a solution of copper, become coated with copper:—when they act as positive pole, they liberate oxygen—and afterwards, when immersed in hydrochloric acid, eliminate chlorine. (Smee.)

Two platinum wires used as the electrodes of a 3-pair battery, in solution of common salt, become more heterogeneous than zinc and copper. (Marianani.)—They are polarized by solutions of sulphate of potash or lime, iodide of potassium (most strongly in this), sal-ammoniac, chloride of barium, nitrate of potash, baryta, or lime, tartrate of potash, or acetate of lime. Again, if litmus or turmeric paper be moistened with any of these solutions, and the electricity of the machine made to act upon them by means of two platinum wires, till decomposition becomes manifest by change of colour, the platinum wires, when connected by the galvanometer, will give a secondary current; so likewise if, after the decomposition, the platinum wires be replaced by fresh ones. (Henrici.)

Two platinum wires, exposed in a solution of sal-ammoniac to the primary current, exhibit the secondary current in another liquid also, even if the part which was immersed in the first solution be cut off; it is then however weaker, and the more so in proportion to the distance from the solution at which the wires have been cut off. The longer the primary current is continued, the more powerful is the secondary current. If the primary current has been continued for thirty minutes (longer duration avails nothing), the wires retain their polarization for several days; it is weakened by rubbing the wires. (De la Rive.)

Conductors polarized in sal-ammoniac excite secondary currents of various strengths in the following order, beginning with that which acts most powerfully: Peroxide of manganese, graphite, charcoal, platinum, gold, silver, copper, brass, iron, tin, lead, zinc. (Pfaff, *Schw.* 53, 395.)

If two silver wires be made to act for twenty-four hours on solution of sulphate of potash, the negative wire ceases to evolve gas as soon as the circuit is broken; but the positive wire evolves as much, if not more than before. If the positive wire be then introduced into that arm of the U-tube which previously contained the negative wire, and this into the positive arm, the evolution of gas still continues on the positive wire, but more feebly; in an unelectrified solution of sulphate of potash, the wire does not evolve any gas.—When zinc is used as the positive and iron as the negative pole in solution of sulphate of potash, and the battery continues in action for about twenty-four hours, the zinc wire gives no more gas after the circuit is broken; but the positive iron wire often continues to evolve gas for half an hour, the quantity increasing as the iron wire is brought nearer to the zinc wire; metallic contact of the two wires has, however, no influence on the evolution of gas. The iron wire, when taken out of the liquid and again immersed, continues to evolve gas, but does not produce any such effect in an unelectrified solution of sulphate of potash: fresh iron wire liberates no gas, even from the electrified solution. (Hisinger & Berzelius, *Gilb.* 27, 287.)—This enigmatical result was observed by Pfaff in solution of sal-ammoniac. (*Schw.* 53, 77.)

Iron, copper, or zinc wires, exposed in caustic potash to a weak primary current, afterwards give a strong secondary current.

If the cups (*App.* 2) contain alcohol, and the lead wire *o* and copper wire *p* are connected for some hours with the poles of a 20-pair battery, while the silver plate *g* immersed in *a*, and the silver plate *i* immersed in

b touch one another at *h*,—then, on connecting the two silver plates with the galvanometer, and dipping them into solution of common salt, the plate which has been immersed in the positive cup appears more positive than tin, and that which has been immersed in the negative cup almost as negative as gold. The oftener the silver has been thus treated, the more quickly does it assume this condition; by wiping and drying the plates, the peculiar state is for the most part destroyed. Gold and platinum behave like silver; lead, tin, copper, and brass may in this manner be made more positive than zinc; in iron the effect is not produced without much greater difficulty. But when copper or brass which has been rendered positive is wiped, it becomes more negative than in its natural state. (Marianini.)

If a strip of zinc in the circuit of the voltaic battery conducts positive electricity into boiled water, the cathode being formed of platinum, the pair soon becomes indifferent; and after the battery has worked for some minutes, a secondary current shows itself (in which, therefore, positive electricity goes from the zinc through the galvanometer to the platinum); but it soon comes to nothing, and remains so as long as the circuit is closed.—If, on the contrary, the positive electricity flows through the platinum into water freed from air, the zinc becomes ten times more positive than in its natural state, or the secondary current is ten times as strong as that which would be excited by zinc with platinum and water not previously electrified. (Buff.)

Also, when several plates or wires of the same metal are made to alternate with layers of the same liquid, and the current of a battery sent through the whole—then the circuit broken, and the two outermost plates or wires connected by means of a galvanometer—a current in the opposite direction to the former passes through the galvanometer. This is the principle of Ritter's *Charging Pile* or *Secondary Pile*, which laid the foundation of the theory of secondary currents. In this instrument a number of plates, all of the same metal, were disposed in alternate layers with moistened pieces of paste-board, and subjected to the current of a voltaic battery. Faraday constructed a pile of this nature with plates of platinum and pieces of paper saturated with yellow solution of sulphuret of potassium. Sir H. Davy constructed a similar apparatus of six bent pieces of metal, the ends of which dipped into six vessels containing solution of nitre. With zinc the secondary current was stronger than with platinum, and its force was generally greater as the metal was more oxidable and the solution more concentrated. When water was used instead of solution of nitre, it was very weak. If the six bent pieces of metal consist half of copper and half of zinc, and a battery of fifty pairs acts on the arrangement, in such a manner that positive electricity always enters the liquid through the copper ends, the secondary current is four times as strong as when the positive electricity enters by the zinc ends,—because, by this arrangement, acid is collected round the zinc and potash round the copper (p. 389). (H. Davy, *Comp.* Marianini, *Ann. Chim. Phys.* 38, 5.)

If an electric current be conducted through three decomposing cells filled with water, till the polarization has attained its maximum, and the two electrodes connected through the medium of a galvanometer, after the removal of the battery,—the deflection amounts to 15° when the electrodes and partitions consist of platinum, to 5° when they are formed of copper, and to 2·5° when they are formed of zinc. (Buff.)

Metals may likewise be polarized in a simple galvanic circuit. Silver

placed for some time in contact with zinc in dilute sulphuric acid appears positive towards silver not so treated; so likewise with gold. Gold which has been in contact with zinc in hydrochloric acid is positive towards lead, but becomes negative in thirty seconds, and even when left alone in the acid, soon loses its positive character. If one end of a gold plate in contact with zinc, be dipped into a cup containing hydrochloric acid, and the other end in contact with graphite, into another cup containing the same liquid, the former end of the gold is found to be much more strongly positive towards platinum than ordinary gold; the other end is negative towards platinum. The same phenomena are exhibited by silver. The polarization of gold is destroyed by exposure to the air, but is retained for months when the metal is wrapped up in paper. Other metals exhibit somewhat similar properties, but more feebly and less definitely.

Platinum which has remained in contact with zinc in oil of vitriol till the maximum of effect has been produced, afterwards exhibits positive reaction towards copper. (Buff.)

Copper remains bright in sea-water when connected with zinc by means of a platinum wire. If the platinum wire be cut through after forty-three days (a few days are not sufficient), the copper, notwithstanding its separation from the zinc, remains bright for a considerable time, twenty days at least; but in fresh sea-water it would be oxidated—so likewise would a fresh plate of copper in the original sea-water. (Van Beek.)

Charcoal and porous coke in contact with amalgamated zinc in dilute sulphuric acid, do not eliminate hydrogen gas but rather take it up, and thereby acquire the power of coating themselves with copper when immersed in a solution of that metal. (Smee.)

Partitions or Interposed Plates.

When the electric current, instead of passing through one single portion of liquid, is made to traverse several portions, connected by metallic plates or wires—the so-called *Partitions* or *Intervening Plates*—or, what comes to the same thing, separated by partitions into a number of *Decomposing*, or *Intervening*, or *Retarding Cells*,—then, if the current has sufficient tension to overcome the resistance, decomposition takes place in each cell. Every surface of the partitions which is turned towards the anode or positive pole, acts as a cathode or negative pole,—and the cations, such as hydrogen or metals, are liberated upon it; and every surface turned towards the cathode or negative pole acts as an anode or positive pole, on which the anions, such as oxygen, chlorine, &c., are evolved. When the tension of the current is sufficient to overcome the increased resistance, the quantity of the products of decomposition obtained in each of the individual decomposing cells is the same as would be yielded by a single cell; and therefore the sum total of the products of decomposition increases in direct proportion to the number of decomposing cells. But with a current of less intensity, the greater the number of cells, the smaller is the amount of decomposition produced in each; and when the number is increased beyond a certain limit, decomposition ceases altogether, and the electric current is stopped. If the intervening plates consist of metals which have a strong tendency to attract oxygen, chlo-

rine, and the other anions of the liquid, this affinity facilitates the decomposition, and renders it possible even with currents of comparatively low tension. But whether the decomposition be strong or weak, its amount in any one cell is exactly the same as in any other.

[According to the theory already laid down (p. 433), the electric fluids do not pass through the liquid, but combine on entering it with its constituent elements. If the two cups *a*, *b* (*App.* 2) are filled with water, and connected by the platinum wire *g h i*, the platinum wire *o* being connected with the positive pole of the battery dipping into *a* and the negative wire *p* into *b*,—the positive electricity which issues from the wire *o* combines with oxygen, and the negative electricity issuing from the wire *p* with hydrogen. The latent electricity or caloric in the wire *g h i* is resolved into negative electricity which unites at *g* with the hydrogen there evolved by atomic transposition, and positive electricity which combines at *i* with the oxygen there eliminated. Thus, oxygen gas is evolved at *o* and *i*, and hydrogen at *g* and *p*; and moreover, the quantity of oxygen gas in *a* is exactly the same as that in *b*, because the positive and negative electricities act in equal proportion;—consequently, equal quantities of water are decomposed in *a* and *b*. For similar reasons, the quantity of hydrogen gas is the same in both cells. As with two cells, so likewise with a greater number: in all cases, the latent electricity of the partitions is decomposed. For every atom of oxygen liberated in the first cell by the positive electricity proceeding from the pole, an atom of hydrogen passes over to the first partition, and there unites with the corresponding quantity of negative electricity; so that the quantity of positive electricity transferred from the first partition to the oxygen of the second cell is equal to that which passes from the wire *o* to the oxygen of the first cell, and the number of atoms of oxygen set free is the same in both places, &c. &c. The decomposition of caloric in the partitions might be expected to produce a fall of temperature in them; but this effect is more than compensated by the development of heat which accompanies the decomposition of water (*vid. seq.*).]

Quantity of the Products of Decomposition.

In any one of the decomposing cells, the quantity of detonating gas evolved is the same as in any other. If the current be first passed through a voltameter, then divided into two parts, each of which passes through a separate voltameter, the last two together yield the same quantity of detonating gas as the first. (Faraday.)

If in a battery of 100 pairs, the contiguous zinc and copper plates be separated at three or four points, and decomposing cells filled with water interposed at those points, the quantities of detonating gas evolved in all these cells will be equal. (Marianini.)

Three decomposing cells being filled with dilute sulphuric acid—negative electricity conducted into all three by platinum, but positive electricity, on the contrary, into the first by platinum, into the second by copper, and into the third by zinc—the same quantity of hydrogen gas is evolved on the platinum in all three cells. At the same time, a large quantity of hydrogen is evolved on the zinc [by pure chemical action], and does not appear to diminish when the circuit is closed; the copper dissolves without evolution of gas. The same quantity of gas is likewise obtained in all the cells when they are filled with hydrochloric acid—and the cathodes are formed of platinum, the anodes of platinum, silver, and

zinc—excepting that the chloride of silver, which is continually forming, impedes the current more and more. (Faraday.)

Tension and Quantity of the Electric Current.

The smaller the number of pairs of plates of which a battery consists, even when the plates are very large, the more is the quantity of the current diminished by the introduction of a partition in the decomposing cell. If the current of a strong battery be weakened by the interposition of a number of decomposing cells, to such a degree that its action on the magnetic needle does not exceed that of a battery consisting of fewer pairs, the current of the latter will be much more weakened by the interposition of a single partition in the liquid which it traverses, than the current of the already weakened battery would be by the introduction of one partition more. (De la Rive.) [The quantities of the two currents are equal, but their intensities different.]

A battery of 40 pairs, which when connected with one voltameter yields 22·8 cubic inches of detonating gas, gives in the same time when 2 voltameters are used, 21 cub. in. in each, or 42 cub. in. in all. In the former case, 88·4 atoms of zinc are consumed in the whole for each atom of water decomposed; in the latter, only 48·3 atoms. But with a battery of only 20 pairs, one voltameter yields 52 cub. in. of detonating gas, with a consumption of zinc amounting to 34 atoms; and with two voltameters, only 14·6 cub. in. are evolved in each, or 29·2 cub. in. in the two together, the consumption being 97 atoms of zinc for every atom of water decomposed. (Faraday.)—With 10 pairs and three or four decomposing cells containing water and connected by platinum, the current is so much weakened that the water is no longer visibly decomposed. (Faraday.)

If a cup-apparatus consisting of eight pairs of zinc and copper in solution of common salt produces a deviation of 12° in the electrometer with the assistance of the condenser—and if between each two contiguous cups there are placed six other cups filled with water and connected by bent copper wires, so that there are 48 inactive cups interposed between 8 active ones,—the battery still exhibits a force of 12°; but on closing the circuit, the current is so feeble that it excites no convulsions in frogs, and scarcely decomposes water: when 60 inactive cups are interposed, no decomposition takes place. (Marianini.) [The quantity is sensibly diminished; the intensity which, doubtless, when the circuit is broken, does not attain its maximum till after a considerable time, remains the same.]

Number of the Decomposing Cells.

The quantity of the current decreases as the number of decomposing cells is increased; but the first cell weakens the current more than the second, the second more than the third, and so on. (Matteucci, De la Rive, Faraday, Buff.)

If the exciting cells contain zinc and platinum with dilute sulphuric acid, and the decomposing cells, platinum plates with dilute sulphuric acid, the following effects are observed, varying according to the number of the exciting cells E and the decomposing cells D:—1 E and 4 D: current very weak;—1 E and 1 D: still no perceptible decomposition of water;—3 E and 2 D or 6 E and 4 D: very feeble current, no visible decomposition;—2 E and 1 D: slight decomposition, soon ceasing;—4 E and 2 D or 6 E and 3 D: no visible decomposition;—5 E and 2 D: slight

decomposition;—3 E and 1 D: decomposition;—6 E and 2 D: no visible decomposition. When a small quantity of nitric acid is mixed with the dilute sulphuric acid of the decomposing cells, the current becomes stronger, because the hydrogen of the water can then combine with the oxygen of the nitric acid. The current is likewise increased by the addition of a little nitric acid to the liquid in the exciting cells, because the tension is thereby augmented, and most of all by the addition of nitric acid both in the exciting and the decomposing cells. The current is not increased by strengthening the sulphuric acid in the two kinds of cells. Hydrochloric acid in both cells produces a stronger current than sulphuric acid, but not so strong as nitro-sulphuric. (Faraday.)

If in a battery of 10 pairs of platinum and amalgamated zinc in dilute sulphuric acid, one of the zinc plates be replaced by a platinum plate, and an exciting cell thereby converted into a decomposing cell, the development of hydrogen gas, and therefore also the current, is reduced to $\frac{1}{3}$ of its former amount,—and to $\frac{1}{10}$ when two zinc plates are replaced by platinum plates, and therefore the circuit is made to consist of eight exciting and two decomposing cells. In all three cases, however, the quantity of hydrogen gas evolved is the same in all the cells. (Daniell.)

If there be disposed one above the other: a zinc plate, a piece of cloth moistened with water, copper 1, wet cloth, copper 2, wet cloth, copper 3,—and the strength of the current be equal to 1 when the zinc is connected by the galvanometer with copper 1,—it will be reduced to $\frac{1}{2}$ on connecting the zinc with copper 2, and to $\frac{1}{3}$ when the connection is made with copper 3. If a copper and a zinc plate be immersed in a trough filled with dilute sulphuric acid, and kept constantly at five inches distance,—then if the deflection $= 3°$ when no partition is interposed, it will be reduced to 1° by the interposition of one plate of lead between the copper and zinc, to 35′ by two, to 20′ by three, to 15′ by four, and almost to nothing by five partitions of lead. (Marianini.)

The small quantity of electricity excited by one pair of plates in water passes through four decomposing cells containing nitro-sulphuric acid without much diminution; but the larger quantity excited by one pair of plates in dilute sulphuric acid is proportionally much more weakened—so that when made to traverse four decomposing cells, it does not exceed the current excited by water. (Buff.)

If the quantity of the electric current is to remain the same when passed through two decomposing cells as when passed through only one, the number of pairs of plates must be doubled. For, according to Ohm's formula (p. 414).

$$Q = \frac{n\,A}{n\,R + r}$$

r denoting the resistance of one decomposing cell; and when the number of pairs and of decomposing cells is doubled, we have

$$Q = \frac{2\,n\,A}{2\,n\,R + r + r}$$

which is the same as the preceding formula. Hence, each decomposing cell requires an equal amount of penetrating force. (Buff, *Pogg.* 54, 108.)

The quantity of the current with a given number of pairs and of decomposing cells may be determined as follows. Let $\frac{A}{L}$ be the observed strength of the current of a single pair metallically connected without any

decomposing cell; n the number of pairs; m that of the decomposing cells; a the ratio of the resistance of a decomposing cell to that of an exciting cell, which ratio varies greatly according to the nature of the liquids employed in the exciting and decomposing cells: then (Buff),

$$Q = \frac{A}{L} \cdot \frac{n}{n + m\,a}$$

In the following experiments pairs of zinc and copper, and electrodes and partitions of copper were employed. In series A, the liquid of the exciting cells, and likewise that in the decomposing cells, is water (in this case $\alpha = 1{\cdot}35$; and with water of the utmost degree of purity, α would be 1·4 with partitions of copper, 0·7 with partitions of zinc, and 2·0 with partitions of platinum.)—In series B, the liquid in the exciting cells is dilute sulphuric acid, that in the decomposing cells, water (in this case $\alpha = 0{\cdot}91$).—In series C, the exciting cells contain water, and the decomposing cells dilute nitric acid (in this case $\alpha = 0{\cdot}09$.)—e denotes the number of exciting cells,—d that of the decomposing cells,—g the deflection of Gourjon's galvanometer, which gives the quantity of the current directly,—b the deflection calculated by the preceding formula.

A.				B.				C.			
e.	*d.*	*g.*	*b.*	*e.*	*d.*	*g.*	*b.*	*e.*	*d.*	*g.*	*b.*
1	1	5·1°	5·2°	1	1	12·5°	12°	1	1	18·2°	18·3°
1	2	3·2	3·3	1	2	6·0	6	1	2	18	17
1	3	2·3	2·4	1	3	4·0	4	1	3	16	15·8
2	1	7·5	7·3	2	1	23·8	23·7	2	1	19	19·1
2	2	5·0	5·2	2	2	11·5	12	2	2	18·5	18·3
2	3	3·5	4·0	3	1	34·2	35·2	2	0	20	20
3	1	8·5	8·4	3	3	11·4	12				
3	2	6·5	6·4	4	1	45·8	46·4				
3	3	5·0	5·2	4	2	22·6	23·7				
4	3	6·3	6·1	4	3	15	15·9				
5	3	7·0	6·7	5	1	58	57·5				
5	0	12·2	12·2	5	2	28·4	29·5				
				5	3	19·0	19·8				
				9	3	35·2	35·2				
				10	1	121·0	109				
				10	2	57·0	57·5				
				10	3	39·6	39				
				10	0		1104				

Chemical Nature of the Liquid and of the Interposed Plates.

The main source of the resistance exerted by the decomposing cells is this—that the liquid contained in them must be decomposed: in addition to this, there is also the less powerful resistance arising from the polarization of the intervening plates, which takes place after long continued action of the current. (Buff.)

The more easily decomposible a liquid is in its own nature, and the greater the affinity of the intervening plates for the elements of that liquid, the less is the resistance.

With 100 pairs of plates, four decomposing cells, and platinum partitions, the resistance of the decomposing cells is smallest when they contain concentrated nitric acid; then follow in order: hydrochloric acid, dilute sulphuric acid, oil of vitriol, saline solutions, and lastly, aqueous solutions of ammonia and potash, which do not offer much more resistance than saline solutions. (De la Rive.)

If two decomposing cells with platinum partitions contain two liquids of unequal decomposibility—*e. g.*, water and dilute sulphuric acid—the current passes through them more easily when the positive electricity of the latter is conducted into the liquid of least conducting power, *i. e.*, the water, and the negative electricity into the dilute acid, than in the contrary case. (Matteucci.)

The current of a single pair of zinc and copper in water or dilute sulphuric acid, is completely stopped by three or four decomposing cells with copper partitions, when the decomposing cells are likewise filled with water or dilute sulphuric acid. But if a quantity of nitric acid be added to the latter, sufficient to produce a slight action upon the copper, the current will not be greatly weakened, even by a considerable number of decomposing cells: the copper will be most attacked at that part from which the positive electricity passes from it to the liquid. (Buff.)

The current of one pair of zinc and platinum in dilute sulphuric acid is not perceptibly weakened by three decomposing cells containing dilute sulphuric acid, when the partitions consist of ordinary zinc plates; but when these plates are amalgamated, a considerable diminution of power ensues. Partitions of copper give free passage to the current at first, but stop it completely after a few minutes, probably because they become polarized. On turning one of these copper plates round, the current is reproduced for a short time. (Faraday.)

If the decomposing cells contain dilute sulphuric acid, the current is most impeded when the electrodes and interposed plates consist of platinum; then follows lead, then copper, then tin, then cadmium. If a zinc plate enclosed between two moist conductors, be placed between a pair of plates of a voltaic battery, the current is much less weakened than it would be by a copper plate introduced in a similar manner. (De la Rive.)—Decomposing cells containing dilute sulphuric acid offer the greatest resistance to the current when the electrodes consist of platinum; then follows copper, then zinc. If, on the contrary, the cells contain ammonia, copper and zinc produce the same amount of resistance.

Volume and Surface of the Liquid.

If the current of a battery of 100 pairs be passed through decomposing cells by means of platinum plates, each of which presents a square inch of surface to the liquid on either side, the strength of the current is the same, whether the partitions are placed at the distance of a foot or of only four lines from each other; but when the thickness of the interposed liquid exceeds a foot, while its section is only one square inch, the current diminishes. Consequently, the loss of the current in its passage through the liquid is almost as nothing [or in other words, the length of the portion of liquid throughout which atomic transposition must be effected, is almost without influence], and the principal loss is sustained in the passage of the electric fluids between the plates and the liquid [or in the decomposition of the liquid, which must take place if the current is to pass]. (De la Rive.)—Faraday likewise found no difference.

The current passes more easily when the partition is nearer to the anode than when it is nearer to the cathode. (Matteucci.)

Even when the interposed platinum plate is nearly a foot long and the polar wires are only three inches distant from it, gas is evolved over the whole surface of the platinum plate. When the decomposing cells

are connected by wires instead of plates, the evolution of gas becomes less, in consequence of the diminished surface. (De la Rive.)

Particular Cases.

When a series of rapidly alternating currents is made to pass, by means of the commutator, from a Daniell's constant battery through two cells filled with dilute sulphuric acid, the following effects are observed, varying according to the nature of the metal of which the electrodes and interposed plate are formed:

With platinum, the alternating current is much less weakened than a current which passes constantly in the same direction (and when Clarke's magneto-electric apparatus is used—if 40 alternating currents follow one another rapidly in a second, and the platinum plates present a large surface, a slight diminution takes place just at first; but when the surfaces, in consequence of the formation of pulverulent platinum, have become more susceptible of oxidation and reduction, the current suffers no further diminution).—With copper, the alternating current exhibits nearly the same quantity, and with tin and cadmium exactly the same, as in the case of metallic connection without decomposing cells; whereas the continuous current, under the same circumstances, is more or less weakened. Lead, which checks the continuous current almost as much as platinum, and at the same time becomes covered, on the side by which the positive electricity passes into the liquid, with a white crust [sulphate of lead?], which impedes the passage of the current, and does not appear to be reduced by hydrogen,—offers nearly twice as much resistance to the passage of the alternating current, because, by the action of such a current it becomes coated with this white crust on both sides. A similar white crust [nitrate of lead?] is produced in nitric acid diluted with an equal quantity of water.—In solution of sal-ammoniac, platinum weakens the alternating current less than in dilute sulphuric acid; chloride of platinum is alternately formed and decomposed by the hydrogen. (De la Rive.)

If a cracked glass tube, closed at bottom and filled with solution of nitrate of silver, be immersed in a glass vessel filled with water, and one of the polar wires dipped into each vessel, electric action takes place through the crack, and decomposition ensues, though but slowly—oxygen gas being evolved at the positive wire and on the side of the crack towards the negative wire (peroxide of silver being at the same time deposited on the positive wire), and silver being reduced on the negative wire and on the side of the crack towards the positive wire (no evolution of hydrogen takes place). The crack acts like a solid conductor, through which, on account of its narrowness, the decomposition of the liquid or the transference of the liberated elements cannot take place. (Grotthuss, *Schw.* 28, 315.)

Union of Opposed Batteries.

[To the theory of interposed plates likewise belong the cases in which two galvanic batteries are connected together with their plates in inverse order, so that their currents act in opposition to one another. In this arrangement, the exciting cells of each battery act as decomposing cells to the other. The current of the one battery has to overcome not only the resistance which the liquid in the cells of the other battery offers to

its decomposition, but likewise the resistance arising from the affinity of the electro-positive metal of the second battery for the anions of the liquid. Unless therefore the intensity of one of the currents far exceeds that of the other, little or no electric force appears to result from such combinations. In every case, it is not the quantity but the intensity of the individual currents that determines the result.]

When a battery of four pairs of zinc and copper in salt water, which by itself produces a deflection of 30°, is oppositely connected with a battery of four zinc and copper pairs in water, which gives a deflection of only 6°, the deflection is reduced to nothing. (Marianini.) [The salt water increases the quantity, but not the intensity of the current; hence the result.]

If five zinc and copper pairs A in cells are oppositely connected with five other pairs B, no current shows itself, even though the plates in A are immersed in spring water six times as deep as those in B. If hydrochloric acid be then added to the water in A, no current is at first apparent; but after a time, a current is produced and gradually increases till it produces a deflection of 0·45°, its direction indicating that the pairs in B which are immersed in only a small quantity of water, are more than a match for the pairs in A, although the five pairs A in water acidulated with hydrochloric acid, produce by themselves a deflection of 44·7°, and the five pairs B in spring water, a deflection of only 1·4°. (Fechner.)

If two batteries of equal numbers of plates, A zinc and copper, B zinc and tin, are oppositely connected—spring water being used in both, A is found to have the advantage: the current even becomes stronger the higher the cells in B are filled with water, a still further increase taking place when hydrochloric acid is added to the water in the cells B. (Fechner.) [The tension of zinc and copper exceeds that of zinc and tin; the cells B are therefore decomposing cells.]

Two series of cups A and B, each consisting of five equal pairs of zinc and copper, are oppositely connected. If the cups in A and B are filled with spring water, a slight deflection is at first produced, but soon ceases. On withdrawing a pair from one series, the needle deviates 20°, but soon returns to 0° [in consequence of polarization?] if the circuit be kept closed. The number of pairs in A and B being still five, but the water in A being mixed with $\frac{1}{100}$ of oil of vitriol, A shows a preponderance of 180°,—but this is soon reduced to nothing if the circuit remain closed. If a pair be then withdrawn from apparatus B, and again immersed, a deflection of 50° [from cessation of polarization?] is produced in favour of apparatus A (sometimes no deflection takes place). Even the mere raising and sinking of a pair of plates in B is sufficient to produce this effect, though in a less degree; but the current always ceases after a time, when the circuit is kept closed. If the cells of B contain spring water, and those of A contain water mixed with $\frac{1}{100}$ oil of vitriol, a deviation of 90° is produced at the moment of closing the circuit, but it is soon reduced to nothing. With $1\frac{1}{2}$ or 2 parts of oil of vitriol to 100 of water in A, no deflection is produced. With $2\frac{1}{2}$ oil of vitriol in A, a slight deflection is produced in favour of B. If, however, in this experiment the water of the cells B be renewed, a deflection of 90° in favour of A is produced on closing the circuit, but it sinks to 0 after a minute. Likewise when from 3 to 20 parts of oil of vitriol are mixed with 100 parts of water in A, there is sometimes no current, sometimes a feeble one which soon ceases, the direction being sometimes in favour of the acid cells, sometimes of the water cells.—If the five cells of B contain spring-

water, those of A 100 parts of water with 10 of hydrochloric acid, no current is apparent. When the hydrochloric acid amounts to 15 parts, the deflection is first 0°, then 40° in favour of B, then 0°, and then again a deflection takes place in favour of the water cells: these alternations are several times repeated. With 20 or 25 parts of hydrochloric acid, there is a deflection in favour of B, continuing for some time; with 30 parts of acid, a still stronger deflection in the same direction; but in a second experiment made in the same manner, no current was apparent.—If the cells of B contain spring water, and those of A a mixture of 100 parts of water with from 5 to 20 parts of nitric acid, no current is apparent; with 25 parts of nitric acid, a long continued current of 50° in favour of the water cells; with 30 parts of acid, the same current but weaker.—In most of these experiments, the plates of B may be replaced by platinum wires as soon as the currents have become equal; the current, which may perhaps appear at the beginning, soon ceases. It appears, then, that the deflection is sometimes in favour of the acid cells, sometimes of the water cells—a circumstance which probably arises from slight alterations in the surface of the plates—since, when the number of pairs is the same, the currents produced by acid and water have the same intensity. (Schönbein.)

When the liquid is dilute sulphuric acid, six pairs of zinc and copper are about equal in power to nine pairs of zinc and iron. (Poggendorff.)

Imperfect Partitions.

When a partition divides a watery liquid imperfectly, less gas is evolved on its two surfaces than upon the two electrodes,—because a portion of the current, instead of first passing into the partition, goes round it through the liquid from one electrode to the other.—When the two ends of the galvanometer are immersed in the liquid on which the electric current is acting, a current is produced in the liquid itself. This current is strongest when the ends of the galvanometer are situated in the straight line between the electrodes, and stronger when they are nearer to one electrode or the other, than when they are more in the middle of the liquid. But the current in the galvanometer likewise shows itself when the two ends are immersed at a considerable distance from the straight line between the two electrodes,—almost throughout the whole liquid, if it be two feet in diameter—and at a greater distance from the straight line between the two electrodes, in proportion as the liquid is a less perfect conductor. (De la Rive.)

[The transposition of atoms in the liquid proceeds partly from one electrode to the other round the imperfect partition, whether it be a plate or a wire; and partly from the two electrodes to the partition itself, whose latent electricity it decomposes, causing various products of decomposition to make their appearance on its surface. When the ends of the galvanometer are immersed, the latent electricity in the wire is decomposed, and produces a current. The less easily the liquid conducts, the greater appears to be the distance between the lines in the direction of which the transposition of atoms may take place.]

Movements of Mercury in the circuit of the Voltaic Battery.

When mercury is put into a U-tube half an inch wide, in quantity sufficient nearly to fill it—water poured on the surface of the mercury in

both arms—and the golden polar wires of a voltaic battery dipped into the water,—the surface of the mercury nearest the negative pole becomes covered with oxide, and remains tranquil; but the surface connected with the positive pole evolves hydrogen gas and produces a disturbance in the water, so that light powders, such as sawdust, or small laminæ of mica, move up and down in it, at first to the height of an inch, afterwards to that of a line,—forming a circular zone when the positive arm is placed upright, and when it is placed in a slanting position, collecting on the opposite side and rotating on their axes in the midst of the water.—If the positive wire be made to touch the mercury, the powder immediately moves towards the point of contact, and attaches itself to the wire; if the wire be separated from the mercury, the powder flies towards the sides of the tube and resumes its former motion.—If, while the two polar wires are immersed in the water, a third wire not connected with the battery be dipped into the water of the positive arm, it pushes the particles of the powder aside, and modifies their motion, which ceases entirely as soon as the third wire is brought into contact with the mercury. (Gerboin, *Ann. Chim.* 41, 196; also *Gilb.* 11, 340.)

The same experiment with a U-tube, a quarter of an inch diameter, the columns of water and mercury being two inches high:—The mercury in the negative arm becomes covered with oxide and remains tranquil: that in the positive arm rises, whilst the water insinuates itself by sudden starts continually deeper and deeper between the mercury and the sides of the tube, and then mounts up again. Powder introduced into the water of the positive arm moves in vortices, the motion increasing as the water sinks to a greater depth between the mercury and the surface of the glass. When the circuit is interrupted, the mercury sinks to its former level and again comes in contact with the sides of the tube. If the tube be smeared internally with fat or lycopodium, the water does not sink between the mercury and the glass, and no motion is apparent. If the positive wire be placed at the edge of the tube at a distance of only a quarter of a line from the mercury, that liquid rises up on it and leaves it again, and thus gives rise to continued oscillations in both arms. (Erman.)

If a globule of mercury two or three lines in diameter, be covered with a small quantity of water, and the two polar wires dipped into the latter, in such a manner that the positive wire may be within a short distance of the mercury, that liquid extends itself out in a line till it touches the positive wire—then starts quickly back and becomes rounded on the surface—then extends itself in the direction at right angles to that of the former extension—again becomes round—then again extended—and at length comes in contact with the wire, &c. &c. These motions take place so rapidly that nothing is seen but a shining star, and go on as long as the current continues. When the negative, instead of the positive wire is brought near the mercury, no motion ensues, because the mercury becomes covered with oxide. (Hellwig & Erman, *Pogg.* 32, 289.)

If mercury be covered with a thin film of water, and the lower surface of a round plate of iron placed in contact with the water, so as to adhere to it, the plate being suspended from one arm of a balance, while the other arm is loaded with a counterpoise just sufficient to cause the water to rise in a cylinder under the plate—and the mercury be then connected with the negative pole of a battery of 100 pairs, and the iron plate with the positive pole,—the water which has been elevated in the cylinder spreads itself with a jerk over the whole surface of the mercury, and pulls the plate down with it; but the plate immediately rises again to

nearly the same height as before. The water then moves continually to and fro in the direction of the radii of the iron plate, the mercury at the same time acquiring a slight motion, which is communicated to the balance. On breaking the circuit, the water returns so quickly under the iron plate that the latter is loosened from it.—If, on the contrary, the mercury is connected with the positive pole, the jerk and the diffusion of the water are much less conspicuous; the water does not move, the mercury becomes covered with a film of oxide, and no sudden separation takes place on breaking the circuit. (Erman.)

If the negative wire be made to dip into mercury covered with a small quantity of water, and the positive wire into the water above it near the side of the dish, the mercury rises, at the moment of closing the circuit, to the height of three-quarters of a line under the positive wire, the water at the same time sinking to an equal depth. This state of things diminishes a little while the circuit remains closed, and suddenly passes into the original state as soon as the circuit is broken. (Erman.)

A drop of water into which the positive wire dips, placed upon mercury into which the negative wire dips, flattens itself out forcibly every time the circuit is closed, and spreads itself over the surface of the mercury. On throwing any fine powder into the water, oscillating currents are observed proceeding from the positive wire to the circumference, and thence again to the positive wire. If the positive wire touches merely the highest point of the drop of water, the mercury acquires a continued oscillation, and the water is thrown up and down with great violence, spurting half an inch high up the wire; at the same time it expands and contracts with equal violence in the horizontal direction. When the negative wire dips into the water, and the positive wire into the mercury, the latter fluid becomes covered with a film of oxide which interferes with the motion; the drop of water, however, flattens itself out in the same manner, but does not contract again when the circuit is unclosed. Oil of vitriol, which, in consequence of stronger adhesion, spreads itself over the whole surface of the mercury, collects rapidly round the wire when the ciruit is closed (the wire not touching the mercury), and again spreads itself over the surface of the mercury when the circuit is interrupted. (Erman.)

If a column of mercury three or four lines in length, be drawn up into the middle of a glass tube half a line in diameter, the tube filled on the right and left of the mercury with water, and the polar wires made to dip into the water, the column of mercury becomes elongated, the water insinuating itself between it and the side of the tube: on unclosing the circuit, the water is again suddenly projected from the tube. When the circuit is closed for a longer time, the extremity of the mercurial column next to the negative pole becomes covered with a film of oxide, which breaks after a few minutes, and shrinks up, the mercury approaching the pole by about half a line; then a new film of oxide is formed, and broken, and the mercury again moves towards the negative pole—and so on. The oxide remains attached to the tube. With machine-electricity, nothing of the kind takes place. (Erman.)

If oil of vitriol be poured upon mercury in a basin four or five inches in diameter, and the polar wires dipped only into the acid on two opposite sides of the basin, all the liquid at the positive pole is pressed backwards and heaped up at some distance from it—forming a dam, from the middle of which two currents proceed towards the positive pole, and thence right and left along the sides of the basin towards the dam at the

negative pole. The motion goes on for a quarter of an hour, till sulphur is precipitated and accumulates in the dam. Similar motions are exhibited by aqueous solution of carbonate of potash. (Erman, *Gilb.* 32, 261; graphic representations of the currents are given.)

If mercury purified by distillation and agitation with nitric acid, be placed in a Wedgewood basin, and covered to the depth of a quarter of an inch with oil of vitriol, and the polar wires of a battery dipped at opposite points into the oil of vitriol, but not into the mercury, a quick circular motion takes place in the oil of vitriol, being caused by a strong current flowing from the negative wire, through the mercury, to the positive wire, and continuing as long as the circuit remains closed. The mercury remains bright, and the quantities of acid decomposed and mercury dissolved, are but small. A mass of mercury weighing from 400 to 500 grains, stretches itself out towards the negative wire, and if the wire is not too far off, reaches and amalgamates it. A smaller quantity moves with violence towards the negative wire, and attaches itself thereto.—Even when the film of oil of vitriol is very thin, the motion still takes place, and the film becomes sufficiently thin to exhibit splendid prismatic colours.—In all these cases, the motion of the oil of vitriol proceeds from that of the mercury; the particles of the former which touch the mercury are rapidly carried along its surface, and draw the more distant particles after them. This motion of the mercury consists in a continued radiation of the superficial particles from the point which is nearest to the negative wire, the particles being carried along the surface to the positive wire, and returning along the axis. The resistance which the bottom of the vessel offers by friction and adhesion to the motion of the liquid from the negative to the positive wire, causes the approach of the globule to the negative wire. In a smooth glass dish, therefore, a mass of mercury shows scarcely any inclination to approach the negative wire, although the currents are equally strong; on the other hand, tolerably large globules of mercury may be kept on a dull ground-glass plate inclined towards the positive wire, without running off.—When the mercury is covered with a film of oxide, the motion takes place under this film, and leaves the watery liquid at rest: but it may be detected by the formation of ridges, which often become very long, taking the direction of the polar wire and following all its motions. In other cases, when the film of oxide is very thick, the mercury flattens itself more and more, and the superficial current goes from the circumference to the centre—the internal current, from the centre in all directions to the circumference.

The motion is strongest along the straight line between the two wires—but is perceptible, though in a slighter degree, at a considerable distance from that line. This becomes evident, when a few drops of mercury are situated at the bottom of the oil of vitriol, those beyond the line joining the wires being agitated as well as those on the line.—The rapidity of the motion seems to depend upon the quantity of the current. Nevertheless, the current of a battery of ten thin zinc and copper wires in dilute nitric acid, is sufficient to give motion to mercury under oil of vitriol. The motion is even excited by the current which is produced, when merely the extreme points of a pair of zinc and copper wires are dipped into dilute nitric acid, with which a glass is wetted; in that case, however, the polar wires must be plunged into two deep baths of mercury at the bottom of the oil of vitriol, and placed right and left of the globule of mercury to be moved—so that a large surface may be offered for the passage of the

electricity. The approach of strong magnets has no effect on the motions. (Herschel.)

If two drops of a watery liquid be placed separate from one another on the surface of mercury, and the polar wires dipped into them (this is more difficult to manage with oil of vitriol than with other liquids, on account of its strong adhesion to the mercury), the motion is confined to the portions of mercury covered with the liquid, but takes place in a similar manner. (Herschel.)

Mercury likewise shows currents under other acids, the motion being more rapid as the acid is stronger and more concentrated; they likewise radiate from the point nearest to the negative wire. The same currents are observed in saline solutions, but weaker as the base of the salt is stronger: hence they are weakest under salts of potash, stronger under salts of ammonia, soda, baryta, strontia, and lime; still stronger under salts of magnesia, alumina, and the heavy metals. In aqueous solutions of the alkalis, mercury remains quiet, provided it be not touched by either of the polar wires. (*vid. seq.*)—In solutions of nitrates, besides the current proceeding from the negative wire, another current is observed proceeding from the positive wire, and is often stronger than the former. Between these two opposite currents a zone of equilibrum is observed, sometimes nearer to the positive, sometimes to the negative wire. This positive counter-current may likewise be obtained in most other watery liquids—or at least an indication of it—when the quantity of mercury is considerable, the solution dilute, the negative wire at some distance from the mercury, and the positive wire close to it. If one polar wire touches the mercury, a current proceeds only from the other—and this current is stronger than in the former cases. (Herschel.)

When the positive wire dips into the watery liquid and the negative wire into the mercury, the latter becomes amalgamated, the mercury remains bright, and its currents are visible to the naked eye. If on the contrary, the positive wire touches the mercury, it oxidates so quickly that the currents cannot be seen; but a sudden agitation, proceeding from the side at which the negative wire is placed, followed by flattening of the globule and the formation of protuberances, shows the existence of currents under the film of oxide. The currents likewise become visible when the coat of oxide is removed by a few drops of nitric acid. (Herschel.)

Experiments with a globule of mercury, weighing 400 *grains, placed under solution of sulphate of soda.* If the two polar wires merely touch the solution, a current proceeds from the negative wire only. If this wire be placed merely for an instant in contact with the mercury (whereby a trace of sodium is separated and combines with the mercury), and both polar wires be then immersed in the solution only, the negative current will be accompanied by a positive counter-current of smaller extent but greater velocity. Between these two currents, a wall of liquid is raised in the direction of which oxide of mercury is continually driven from the negative wire, and disappears again as fast as it is formed on the side of the wall next to the positive wire. The positive counter-current is probably caused by the repulsion of the electro-positive sodium by the positive electricity.—If the negative wire be left for some time in ntact with the mercury, and then separated from it, the negative current becomes much less, and the positive much more extended. When the negative wire is left for a still longer time in contact with the mercury,

and then both wires made to dip into the solution without touching the mercury, the negative current ceases altogether, and there remains only a regular circular motion throughout the whole globule, from the side of the positive to that of the negative wire.—After a still longer contact of the negative wire with the mercury (whereby the mercury becomes more strongly charged with sodium), if the two wires are immersed in the solution only, particles of mercury radiate from all points towards that part of the mercury which is nearest to the negative wire—the force with which they are drawn towards this wire appearing to be greater than that with which they are repelled from the positive wire. If the distance between the positive wire and the mercury be then increased by the smallest possible quantity, and the negative wire brought close to the mercury (but without touching it), a film in the form of a circular spot is formed immediately under the latter, and follows the motions of the mercury. When this film is removed, the mercury is driven with violence against the wire, sometimes springing up to the height of 0·2 or 0·3 of an inch.—When a small quantity of sodium is added to pure mercury, the mercury, even though not touched by the negative wire, exhibits the positive counter-current,—and this current is stronger, the greater the quantity of sodium added.—When mercury amalgamated with sodium, either by contact with the negative wire, as above described, or by direct addition of the sodium, is kept for some time in the current (the wires dipping into the solution), it parts with its sodium, and recovers its former property of exhibiting the negative current only. If the mercury which has been in contact with the negative wire, be connected with the positive wire, whilst the negative wire is made to dip only into the solution, rapid currents are at first produced, proceeding only from the positive towards the negative wire. Gradually however currents also arise, proceeding from the negative wire, and extend themselves by degrees, till the zone of equilibrium reaches that part of the mercury which is nearest to the positive wire. At the same moment, the mercury in the neighbourhood of the negative wire begins to oxidate; and after a while, the whole of the mercury becomes covered with a thick film of oxide, which however disappears again completely when the action of the current has been continued for a longer time. (Herschel.)

If, while the mercury is covered with the film of oxide, its connection with the positive wire be broken, so that both wires may remain immersed in the solution only, radiation commences from the negative wire, breaking through the edges of the film, advancing towards the positive wire, and then ceasing. Upon this the negative radiation ceases, and after momentary quiescence, a rapid current sets in from the positive wire.—The mercury in fact takes up sodium by contact with the negative wire; subsequently, by contact with the positive wire, it becomes coated with oxide, while the internal part still contains sodium (for even when the circuit is interrupted, the film of oxide disappears in consequence of the sodium contained in the interior); if the positive wire be then withdrawn, the oxide is reduced by the sodium.—The superficial portion of the mercury thus freed from sodium is carried by the current from the negative towards the positive wire, fresh sodium passes from the interior to the surface, and is removed from the mercury by reducing the oxide; the mercury is then driven towards the positive wire—and so on, till the film of oxide is wholly decomposed. There now remains mercury containing a little sodium, and consequently the positive current is produced. (Herschel.)

If the mercury, covered with solution of sulphate of soda, be left for some time in contact with the positive wire, and then both wires removed from the solution, the mercury acquires a slight irregular motion and evolves a few gas-bubbles. If any metallic wire be then dipped through the solution into the mercury, the latter rushes from all sides towards the wire, on which, at every part which is in contact with the solution, hydrogen gas is evolved. By this galvanic combination between the metal, the sodium, and the liquid, the whole of the sodium becomes oxidized in twelve seconds at most; and if the wire consists of copper or platinum, the mercury recovers its former property of producing the negative current only. A bent wire may also be made to dip with one end into the upper part of the mercury not covered by the solution (at which part no action previously takes place), and the other end into the solution only: hydrogen gas is then evolved upon the latter, and currents are also produced in the mercury, proceeding from the extremity of the first wire towards the circumference. (Herschel.)

Experiments with mercury under alkaline solutions.—When neither of the wires touches the mercury, no current is produced; but if the negative wire has been made to touch the mercury for a short time, or if an easily oxidable metal has been added to the mercury, a positive current is produced when both the wires are dipped into the solution without touching the mercury. Even when only one part of potassium is added to 1,000,000 parts of mercury, the latter exhibits a positive current. This current likewise shows itself rather strongly when one part of sodium is added to 1,200,000 parts of mercury, and very weakly with one part of sodium in 1,600,000 parts of mercury. Ammoniacal amalgam added to mercury gives no motion under aqueous solution of soda. A small quantity of barium-amalgam imparts positive rotation to the mercury. One part of zinc in 100,000 parts of mercury produces a strong positive current under aqueous solution of potash, a weak but perceptible current with 400,000 parts of mercury, a very weak one with 700,000 parts, and none at all with 1,000,000 parts. Very small quantities of iron cause the mercury to rotate. One part of tin or lead, dissolved in 200 parts of mercury, imparts a powerful rotation to that liquid, a feeble current in 667 parts, very feeble in 1000 parts, and none at all in 2000 parts. Antimony causes the mercury to rotate very slowly, probably acting by means of foreign metals contained in it. By taking up bismuth, copper, silver, or gold, on the contrary, mercury does not acquire the property of exhibiting motions in the electric circuit under an alkaline solution. (Herschel.) (Pfaff did not obtain a positive current on adding zinc, tin, or lead to the mercury, and dipping the two wires into the solution only.)

Experiments with mercury under aqueous solution of carbonate of soda.—If an electric current be passed through two equal quantities of mercury under the solution, one being connected with the negative and the other with the positive wire (the latter portion becomes covered with oxide), and the two portions then mixed, the whole behaves like pure mercury, because the oxide produced in the latter portion oxidizes the sodium contained in the former.—When the mercury connected with the positive wire has become covered with oxide, if both wires be removed from the solution, and a piece of potassium, sodium, tin, zinc, iron, or copper, dipped through the solution down to the mercury (the metals are named in the inverse order of the strength of their action,—copper acting feebly, silver and

platinum not at all), the oxide disappears quickly at the point of contact, and that which is at a greater distance from this point flows quickly towards it, and disappears in like manner. (Herschel.)

Experiments with mercury under solution of nitrate of copper. When the positive wire touches the mercury, a current is produced, proceeding from the side on which the negative wire is placed. This current still continues with slight force after both wires have been completely removed: it even becomes gradually stronger, and drives the film which has been formed during electrolization, towards the place at which the positive wire was situated, so that oxide accumulates there while the opposite surface remains bright: at length, the current which proceeds from the negative side becomes very violent, and this spontaneous motion often continues for a long time.—If the negative wire be made to touch the mercury for an instant at two opposite points in succession, while the positive wire touches the solution only, and both wires be then removed from the liquid, these two points form centres from which spontaneous currents issue simultaneously. If the positive wire be left in contact with the mercury (under nitrate of copper?) till a film of oxide has been formed, and the current then made to pass through the liquid only, the film of oxide is driven towards the positive wire by a violent current proceeding from the negative wire. If the circuit be broken after a time, the motion continues still longer. If the mercury be agitated during the motion, so as to scatter the coating formed near the positive wire, spiral currents are produced, moving towards every particle of oxide diffused over the surface,—the liquid being thrown into a state of tremulous motion, till the film of oxide becomes reunited, and a more uniform motion is produced. (Herschel.)

When the mercury is impure, very anomalous appearances are often produced.

Fusible metal melted at the bottom of a boiling solution of sugar, exhibits motion with predominant radiation from the positive wire, when the polar wires are made to dip into the solution; when the sugar solution contains phosphoric acid, the mixture exhibits negative rotation like pure mercury. (Herschel.)

Thirty globules of mercury, from 10 to 100 grains in weight, placed in a flat glass dish, at the bottom of a solution of one part of sulphate of potash in 2000 parts of water, in which are immersed the polar wires of a battery of 1000 pairs of plates, lengthen themselves out—to a greater extent in proportion as they are nearer to the line joining the polar wires—and approach, some to the positive wire, some to the positive pole of the neighbouring globules. No hydrogen gas is evolved, but oxide of mercury moves with violence from the positive to the negative poles of the several globules. The addition of hydrochloric acid to the solution stops the motion. (H. Davy.)

Experiments with mercury under salts of ammonia, potash, baryta, strontia, carbonate of potash, sulphate of soda, or nitre. When the polar wires dip into the solution only, the mercury moves with perceptible elongation towards the positive wire. If the positive wire dips into the mercury, that liquid shrinks together slightly at first, then becomes covered with oxide, and spreads itself out. If, on the contrary, the negative wire dips into the mercury, a sudden flattening of the mercury is produced, and a visible current is formed over its surface from the positive towards the negative wire, then right and left back again towards the positive wire. If the negative wire be now withdrawn from

the mercury, the motion becomes stronger for a time, but ceases when the alkali-metal which has been separated from the solution becomes oxidized.—The currents are weaker in solutions of the salts than in those of the alkalis, and weakest of all in pure water.—Solutions of sal-ammoniac, chloride of potassium, or chloride of sodium, behave in a similar manner, but with certain differences. (Pfaff.)

Experiments with mercury under oil of vitriol or concentrated hydrochloric acid. When the wires dip only into the acid, the mercury moves towards the negative wire, and a perceptible current goes from the negative to the positive wire, and then on both sides back again to the positive wire.—When the positive wire touches the mercury, the motion ceases, and the mercury spreads itself out.—If the negative wire be dipped into the mercury, that liquid contracts, and exhibits a slower and straighter motion. (Pfaff, *Schw.* 48, 190; this memoir contains many other remarkable particulars:—*comp.* Runge, *Pogg.* 8, 106.)

These motions of mercury should be compared with those previously described (pp. 381...384).

Development of Heat in the Galvanic Decomposition of Liquids.

Development of Heat in the Exciting Cell of the simple Galvanic Circuit.

[When an atom of zinc is burnt and enters into combination with an atom of oxygen, about twice as much heat is set free as in the combustion of an atom of hydrogen (p. 292). Now since, according to Faraday's experiments, an atom of metallic oxide does not require for its decomposition a greater quantity of positive and negative electricity than an atom of water, we are led to suppose that in the combustion of an atom of metal, the quantity of negative electricity which combines with the positive electricity of an atom of oxygen is not greater than the corresponding quantity in the combustion of an atom of hydrogen, and that the quantity of positive electricity given up by an atom of oxygen is the same in both cases. That however a much greater quantity of heat is obtained in the combustion of an atom of zinc, may arise either from this —that the heat obtained does not proceed solely from the combination of the two electric fluids, but likewise from heat existing in the zinc in a state of intimate combination, and set free during combustion—or more probably still, perhaps, that of the heat developed by the union of the two electricities, a greater quantity is retained in a state of intimate combination by water than by oxide of zinc. With this is connected the fact, that heat is evolved during the solution of zinc in dilute acids. Now, according to the theory already laid down, this development of heat cannot arise from the combination of the two electricities; for the solution of zinc in acids is attended merely with a transference of negative electricity from the zinc to the hydrogen (p. 342, *c*). Part of the heat thus evolved doubtless arises from the combination of the sulphuric acid with the oxide of zinc produced; but, on the other hand, a large quantity of heat must be rendered latent from two causes;—first, because the sulphuric acid which combines with the oxide of zinc is separated from its state of intimate union with the water,—and secondly, because the hydrogen gas which escapes renders latent a certain quantity of heat of fluidity. Hence the development of heat must be attributed mainly to the escape

of the combined heat either of the zinc or of the water.—A similar evolution of heat likewise takes place when zinc is placed in contact with copper, &c. Hence, in simple galvanic circles, a rise of temperature generally takes place, both in the metals and in the liquid. The evolution of heat must be the same for a given quantity of zinc oxidated, whether the oxidation takes place by ordinary or by electro-chemical action. In the latter case, however, it must be observed that the hydrogen receives its negative electricity, not from the zinc but from the copper, the latent electricity of which—*i. e.* its caloric—is decomposed, and thereby diminished in quantity,—and that the liberated positive electricity goes from the copper through the connecting wire to meet the negative electricity of the zinc, and combines with it in the zinc to form heat. The greater therefore the quantity of heat generated in the zinc, the smaller will be the evolution of heat in the cell. The quantity of heat evolved in the cell would therefore increase as the conducting power of the wire diminished, if the oxidation of the zinc could then go on with equal rapidity; but since the oxidation of common zinc is retarded under such circumstances, and that of amalgamated zinc almost wholly arrested, the contrary result is obtained.]

If an amalgamated zinc plate and a silver plate platinized by Smee's method (p. 419), are immersed in 2 lb. of dilute sulphuric acid, and produce a current in a thick conducting wire of sufficient force to decompose 9 grains of water in an hour, the temperature of the 2 lb. (= 18432 grains) of liquid rises 4·7° Fah. in an hour. If from this we deduct the heat developed by the combination of the sulphuric acid with the oxide of zinc produced, there remains 2·1° Fah. for the rise of temperature due to the current. (Joule.)—[18·432 × 2·1 = 38707·2. Consequently, one grain of water would be heated 38707·2° Fah. or 21504 C°. At the same time, since the current acting for an hour decomposes 9 grains of water, 8 grains of oxygen are transferred to the zinc : $\frac{21504}{8} = 2688$; while, therefore, 1 part of oxygen has been transferred from the hydrogen to the zinc, a quantity of heat has been evolved in the trough sufficient to raise the temperature of 1 part of water by 2688 C° or 4838° Fah. Since the two plates were united by a thick wire, which allowed the negative electricity to pass without hindrance from the zinc to the copper, the heat evolved in the wire may be reckoned as nothing. The difference in the quantities of heat evolved in the combination of 1 part of oxygen with zinc and with hydrogen respectively is (5290 — 3000) = 2290. The experiment just described gave 2688: this excess arises from the circumstance mentioned by Joule himself, that a small quantity of zinc was oxidated by ordinary chemical action.—In a second experiment, in which the two plates were placed only half an inch instead of an inch apart, the rise of temperature in the liquid was 4·4°,—or, after deducting the heat developed by the combination of oxide of zinc with sulphuric acid, 1·85° Fah. [The greater proximity of the plates probably diminished the ordinary chemical action. Calculation as above gives for every 1 part of oxygen which combines with zinc, a rise of temperature in 1 part of water amounting to 2368 C°., which agrees very nearly with the quantity of heat developed by the oxidation of the zinc.]

[Joule explains the development of heat on totally different principles, but appears not to be aware that in his calculations he has taken the quantity of the current for its intensity—a mistake of frequent occurrence.]

Grove's battery gives similar results. When the circuit is closed by

a long thin wire, so that the quantity of the current is diminished, the rise of temperature in the liquid likewise becomes less [partly because the chemical action is slackened, partly because the combination of the electric fluids within the wire develops a quantity of heat which would otherwise have been evolved in the troughs].

In Daniell's apparatus, on the other hand (zinc, dilute sulphuric acid, sulphate of copper, and metallic copper, p. 421), a considerable reduction of temperature takes place. (Joule, *Phil. Mag. J.* 19, 260.) [This deserves attention, inasmuch as heat is evolved during the precipitation of a solution of sulphate of copper by zinc.]

Development of Heat in the Troughs of a Trough Battery.

When a battery consisting of four porcelain troughs filled with dilute nitric acid—each trough containing 10 cells, having a pair of zinc and copper plates immersed in each, and therefore making 40 pairs in all—is left for some time with its poles connected, a rise of temperature takes place in the liquid contained in the cells. In one experiment of this kind, the temperature of the liquid was at first 16·6° C.; in the middle of the trough, containing the positive pole, it rose to 55·5°; in the next to 54·7°; in the third to 53·6°; and in the trough which contained the negative pole, only to 43·2°. (Murray, *N. Ed. Phil. J.* 12, 57.)

Development of Heat in the Decomposing Cell.

[Watery liquids are the only substances, the decomposition of which has hitherto been observed to be accompanied by elevation of temperature. If we suppose (according to p. 494) that of the heat produced in the combination of oxygen and hydrogen, a great part remains united with the water (2,290 parts out of 5,290), then this quantity of heat must be liberated during the electrolysis of the water. For, at the positive poles, the full quantity of heat combines with one atom of oxygen, and at the negative pole, one atom of hydrogen takes up the full quantity of negative electricity,—the heat, which was held in a state of combination by the atom of water decomposed, remains in the liquid in the free state.]

Two gold cups containing water are connected by asbestus, and into one of the cups, in which the positive wire of a battery of 100 pairs is immersed, a drop of a solution of sulphate of potash is let fall: the potash then passes rapidly into the negative cup, and the water is raised in two minutes to the boiling point. When the current acts on a solution of nitrate of ammonia, all the water evaporates in three or four minutes, producing a hissing noise and a white cloud, and the remaining nitrate of ammonia takes fire.—When one of the cups contains strong solution of potash, and the other oil of vitriol, only a slight elevation of temperature is produced. (H. Davy.)

When dilute sulphuric acid is decomposed by Grove's battery, it is converted into oil of vitriol, and becomes so hot, that wood placed under the vessel which contains it is charred. (Grove.)

In the electrolysis of a watery liquid, a greater rise of temperature takes place at the positive than at the negative pole,—because less gas is evolved at the former, and therefore less heat is rendered latent. The evolution of heat is greater when the liquid is divided into a number of separate parts by porous bodies, such as membranes, bundles of thread,

&c. The liquid in a bundle of cotton fibres is more strongly heated than that contained in a glass tube of equal width and length; for the cells in which the liquid is enclosed retard the transmission of the electricity. If the polar wires are inserted into the extremities of a cutting of a water-plant, the water near the wires rises to the boiling point. (De la Rive.)

[Experiments of Prescott Joule (*Phil. Mag. J.* 19, 260).]

Technical Applications of Galvanism.

1. Galvanic Precipitation of a thin Layer of one metal on the surface of another.

Gilding.

This process may be performed upon silver, brass, or copper, but not upon iron. The apparatus consists of a bladder containing dilute acid, in which zinc is immersed, and a jar within which the bladder is placed. The jar contains the solution of gold, together with the metal to be gilt, which is connected by a wire with the zinc. (The gold solution and the metal to be gilt may also be placed within the bladder,—the dilute acid and a cylindrical zinc plate surrounding the bladder being placed in the outer vessel.)—The more dilute the acid, the feebler is the current, and the better does the gilding go on;—*e. g.*, six drops of acid to a glass of water. Sulphuric acid is used for silver, nitric acid with copper or brass. —The gold solution, which is made as neutral as possible, contains 5 milligrammes of gold in a cubic centimetre, and therefore one gramme of gold in a litre (about 2 pounds). A weaker solution gives a darker, and a solution containing copper mixed with the gold a redder gilding.—The metal to be gilt must be either polished or merely cleaned. In the former case, the metal takes the gilding more readily, and the gilt surface has a much greater lustre, and merely requires rubbing with fine linen or with leather to give it a very high degree of polish; in the latter case, the gilding is taken slowly, has a duller surface, and requires to be rubbed with the burnishing steel. Ignited silver takes a finer gilding than that which has not been ignited.

The zinc is attached to a thick copper wire, and this to a silver or platinum wire, which touches at one point the metal to be gilt: this point must however be changed from time to time, otherwise no gold will be deposited upon it. Before the gilding process is commenced, the metal is dipped into dilute acid to free it from all impurities,—silver in sulphuric, copper and brass in nitric acid. If the zinc, contained in a bladder filled with the same acid, be at the same time immersed in the liquid, the gas-bubbles evolved on the surface of the silver or copper will serve to cleanse it still more effectually.

After this the gilding is commenced. The bladder with the zinc being first placed in the gold solution, the circuit is closed by immersing the object previously metallically connected with the zinc. The metal to be gilt, especially if it be silver, must not be left for a moment in the gold solution without galvanic connection,—otherwise it will either not be gilt at all or the gilding will be very bad. If therefore the inside of a vessel is to be gilt, the bladder with the acid and zinc being suspended within it, the gold solution must be poured into the vessel down the sides of the bladder, so that galvanic connection may be immediately formed. The galvanic current must be so weak that scarcely any gas

shall be evolved on the surface of the silver or copper; for any considerable evolution of gas would interfere with the deposition of the gold. A feeble current is particularly necessary when sharp edges occur, for these are difficult to gild. The current is regulated by partially withdrawing the zinc or diminishing the quantity of acid. After remaining for a minute or two in the gold solution, the metal is again immersed in dilute acid; it is likewise advantageous to immerse the zinc and bladder at the same time (for this makes the gilding more brilliant, and ensures a more abundant deposition of gold at the next immersion). The metal is then briskly rubbed with fine linen and dried, then again subjected to galvanic action in the gold solution,—and so on. Polished objects require two or three immersions—unpolished ones, five or six.

Brass requires less gold and takes a redder gilding than silver, the gilding on which is rather of a greenish yellow. The gilding is permanent.

Those parts of an object which are not to be gilt are covered with wax, or washed with gold solution by means of a brush.

The solution of gold when weakened by use is concentrated by evaporation. The bladder, which requires frequent renewal, yields a quantity of gold when burnt to ashes. (De la Rive. *Ann. Chim. Phys.* 73, 398; also *J. pr. Chem.* 20, 157.)

R. Böttger makes use of the following apparatus for gilding and platinizing. A wide cylinder has a hole in the middle of its base, through which there passes a copper wire cemented in with sealing-wax. The part of the wire within the cylinder is formed into a flat spiral, upon which is laid a piece of amalgamated zinc. The cylinder contains very dilute sulphuric acid. In this is immersed a cylinder open at the top and bottom, but tied over at the bottom with a thin bladder. The cylinder contains solution of gold, in which the metal to be gilt is immersed after it has been first connected, by means of a platinum wire wound round it, with the copper wire proceeding from the zinc. (A drawing of the apparatus is given in the memoir.) The gold solution contains one part of chloride of gold, freed as much as possible from excess of acid, in 160 parts of water; or still better, chloride of gold and sodium dissolved in water. Each immersion lasts for a minute at the utmost, and is followed by washing with water and drying, accompanied by brisk rubbing with fine linen and polishing with powdered chalk. Silver requires five or six, steel ten or twelve immersions, lasting from half a minute to a minute. When the silver object is connected with the zinc by a copper wire, part of which dips into the solution of gold, the gilding acquires a strong reddish tint; whereas, when silver or platinum wires are used, it is of a full bright yellow. If the gold solution contains the smallest trace of copper, scarcely any thing but copper is at first deposited upon the silver. Copper also does not show any appearance of gilding for some time, because the red colour of the metal shines through. (The same was observed by Biewend, *J. pr. Chem.* 23, 253.) Brass may be gilt almost as well as silver, tin not so well. German silver gives a coppery kind of gilding, not very beautiful. But watch-springs, pen-knives, &c., may be gilt directly by De la Rive's method. Watch-springs take a very beautiful gilding, when they are freed by hydrochloric acid from the blue film of oxide. On long knives the gilding is not uniform, being thickest at the end next the zinc. Steel, which is to be gilt must be brightly polished without oil; that which has been polished with oil does not take the gold; for it retains particles of

oil closely attached to its surface, so that it is scarcely attached by strong hydrochloric acid. (R. Böttger, *Ann. Pharm.* 35, 221 and 350.)

The bladder recommended by De la Rive reduces a considerable quantity of gold, which gives it a purple colour; a cylinder tied over with bladder at bottom is therefore to be preferred. Only a feeble current is required, and a single drop of sulphuric acid is enough for every ounce of water. If the gold solution reddens litmus, it produces a dirty yellow coating on the silver; hence it must first be exactly neutralized with carbonate of soda. It must likewise be more dilute than Böttger recommends; water must in fact be added to it till a plate of silver dipped into it no longer acquires a black coating, but exhibits a bright yellow colour on being rubbed. When the process is thus conducted, the silver no longer acquires a greenish yellow, but a pure bright yellow gilding; or if it be connected with the zinc by a copper wire, it then takes, as Böttger found, a reddish yellow gilding. Steel pens, freed by dilute hydrochloric acid from their blue film of oxide, may be gilt without the aid of galvanism by simply immersing them in the gold solution neutralized as above with carbonate of soda. Copper may likewise be gilt in a very short time either by ordinary chemical action, like steel, or by the galvanic method. (Elsner, *J. pr. Chem.* 23, 148.)

Walker (*Phil. Mag. J.* 19, 328) makes use of the current of a voltaic battery. The decomposing cell contains a solution of cyanide of gold and potassium; the anod econsists of a plate of gold, and the cathode of the metal to be gilt. As fast as gold is precipitated from the solution on the cathode, fresh gold is dissolved at the anode. A similar method is pursued by Elkington (*Compt. rend.* 13, 998; also *Pogg.* 55, 161), according to whom, gilding goes on more quickly at a somewhat elevated temperature than in the cold.—According to Ruolz (*Pogg.* 55, 162) the following solutions are available for this purpose: Cyanide or chloride of gold in aqueous solution of cyanide of potassium; ordinary ferrocyanide of potassium or red ferrocyanide of potassium; chloride of gold and potassium in aqueous solution of cyanide of potassium, or in aqueous solution of soda; sulphuret of gold in aqueous solution of sulphuret of potassium. The last three solutions are to be preferred—the last, which contains sulphur being the best of all. In this manner, platinum, silver, copper, packfong, and steel may be gilt permanently, beautifully, and of any required thickness. A solution of 1 part of chloride of gold and 10 parts of ferrocyanide of potassium in 100 parts of water, being subjected to the action of a six-pair Daniell's battery, deposits in three minutes, on a polished silver plate, five square centimetres in surface, the following quantities of gold, varying according to the temperature: at 15°, 0·0126; at 35°, 0·0296; and at 60°, 0·063 of a gramme.—The quantity of gold deposited on a brass plate of equal size at 15° in two minutes was 0·012 of a gramme. (Dumas.)

De la Rive's method produces a brilliant gilding, that of Ruolz gives a fine frosted surface which may be made bright by polishing. De la Rive's solution acts partly by ordinary chemical action, because it contains too much gold and is not sufficiently neutralized. The following method gives the best results.—Gold-solution: 1 part of dry chloride of gold and 10 parts of ordinary ferrocyanide of potassium are dissolved in 100 parts of water, filtered from cyanide of iron, mixed with 100 parts of saturated solution of ferrocyanide of potassium, and this mixture is diluted with an equal or double quantity of water: the more dilute the solution the brighter is the frosted gilding produced.—*Liquid in the zinc vessel:*

solution of ordinary ferrocyanide of potassium and common salt:—solution of common salt alone acts more quickly; but for gilding silver, the solution must not contain too much common salt, otherwise the silver will be blackened by the formation of chloride. All acid is to be avoided; it gives too strong a current. It is advantageous to have the gold solution and the liquid in the zinc vessel of the same specific gravity, in order that they may not mix too easily. For the same reason, the level of the two liquids ought to be the same. The zinc must not be amalgamated, otherwise chloride of mercury will be introduced into the gold solution, and may be reduced on the metal.—*Vessels:* For gilding small objects the gold solution may be contained in a glass tube, open at both ends; for larger objects, in an inverted bell-jar, furnished with a tubulure. The lower end of the glass tube or the tubulure of the bell-jar is tied over with linen, and a layer of kaolin or common clay, free from lime, one centimetre in height, and moistened with solution of common salt, placed at the bottom of the tube or jar. If instead of glass, vessels of earthenware are used, in which endosmose is stronger than in clay,—then, either the inner and outer liquids must have the same composition (with the exception of the gold contained in the inner), or the earthen vessel must be enclosed within a bag of muslin filled with moist clay, so that the vessel may be surrounded with a coating of clay one or two centimetres in thickness.—The brass, copper, or silver, which is to be gilt, is well burnished and then thoroughly cleansed (*decapé*) by rubbing it with lamp black moistened with concentrated nitric acid and spread upon linen—then dipping it quickly into water, then again rubbing it—and so on:—when perfectly clean and bright, it is well dried. While the gilding is going on, the object is frequently turned, so that the deposit of gold may be uniform. If the deposition goes on too slowly, an additional quantity of common salt is added to the liquid in the outer vessel containing the zinc.—Warming the outer vessel in a water-bath to 20° or 25° (68° or 77° Fah.). likewise accelerates the gilding but diminishes its lustre. If any of the gold solution penetrates into the outer vessel, and gold is in consequence precipitated upon the zinc, it must be removed. A thin deposit of gold makes its appearance in ten minutes; to produce a thick deposit, several hours are necessary, The gilding on silver is first greenish, then yellow, then after twelve hours, reddish yellow. Brass and bronze take the gilding much more quickly. Finally, the gilt object is washed with dilute sulphuric acid, which removes any iron which may perchance have been precipitated, and then rubbed with linen. The gilding holds very fast. (Becquerel, *Compt. rend.* 14, 135.)

When a copper plate is to be etched,—instead of covering it with the ordinary etching ground, it may be gilt by De la Rive's method, and then the gold removed with the needle; in this manner much finer lines are obtained. Moreover, since the gold remains attached to the surface, the plate may be corrected, if the first impression should be faulty. (De la Rive, *J. pr. Chem.* 22, 376.)

Platinizing.

This may be done upon silver, brass, or copper. The apparatus is the same as that of Böttger for gilding. The platinum solution used consists of 1 part of chloride of platinum in 160 parts of water—or better, 1 part of chloride of platinum and 1 part of common salt in 160 of water. The latter solution yields a sufficient deposit after three immersions; whereas

with the former, six immersions are necessary, and the coating of platinum is rather grey than white. Copper which has been platinized is afterwards well adapted for gilding. This may be done with objects obtained by the electro-type process,—a copper wire being fastened to the centre of the hinder surface, that surface covered with wax, the front surface freed from every trace of oxide by rubbing with dilute hydrochloric acid and fine washed sand,—then, by the preceding method, first platinized and afterwards gilt. Any part on which the oxide still remains will not be coated, and must afterwards be cleaned with sand and acid. (R. Böttger.)

For platinizing by the current of a six-pair Daniell's battery, it is best to use a solution of chloride of platinum and potassium in potash. The operation goes on as quickly as gilding. But from a solution of 1 part of cyanide of platinum and 10 parts of yellow ferrocyanide of potassium in 100 parts of water, platinum is very slowly precipitated, even when assisted by the application of heat. (Ruolz & Dumas, *Pogg.* 55, 164.)

Silvering.

Copper and brass may be silvered in the above apparatus by means of a solution of 1 part of fused nitrate of silver (lunar caustic) in $5\frac{1}{3}$ parts of aqueous ammonia; but the first immersion must not last longer than a second. (R. Böttger.)—Walker proceeds, according to the method described on page 499, with a solution of cyanide of silver and potassium as the electrolyte, and a silver plate as the anode.—According to Ruolz, who likewise uses cyanide of silver and potassium, silvering may be produced on gold, platinum, copper, bronze, brass, iron, cast-iron, steel, and tin, and is very permanent.—A solution of 1 part of cyanide of silver and 10 parts of ordinary ferrocyanide of potassium in 100 parts of water, may also be used. (Dumas.)

Coppering.

A solution of cyanide of copper in cyanide of potassium or sodium yields a coating of copper when acted upon by the current of an eight-pair Daniell's battery,—but the deposition of the copper is very slow. (Ruolz.)—In a similar manner, metals may be coated with lead, cobalt, or nickel. (Ruolz.)

Tinning.

Clean copper or brass, in contact with cuttings of tin in a boiling solution of peroxide of tin in potash, becomes covered in a few minutes with a white permanent layer of tin. (R. Böttger.)—Bronze may likewise be tinned in this manner. With electro-positive metals, on the contrary, such as iron or zinc, the current of a battery is necessary. (Ruolz.)—On this principle depends the tinning of brass pins by disposing them in alternate layers with tin plates, and boiling the whole in a solution of cream of tartar.

Zinking.

Copper or brass cleaned with dilute hydrochloric acid, and placed in close contact with granulated zinc, in a boiling saturated solution of sal-ammoniac or a solution of chloride of zinc, acquires in a few minutes a specular covering of zinc. Cream of tartar, in place of sal-ammoniac, does not occasion a deposit of zinc. (R. Böttger, *Ann. Pharm.* 34, 84; 39, 172.)—By means of the electric current of a battery, iron wire, iron plate,

cast-iron, &c., may also be coated with zinc, and preserved from rust. (Roslz.)

2. Electrotype.

Wach and others discovered some time ago that under certain circumstances copper may be deposited in a coherent state by galvanic action. But Jacobi (*Electrotype*, Petersburgh, 1840; abstr. *Polytechn. J.* 75, 110)—and Spencer, as it appears, at the same time—showed (*Polytechn. J.* 75, 34; 77, 343) that copper thus precipitated in the solid state on conducting bodies, adapts itself exactly to all the depressions of their surfaces, and when separated presents an exact impression of them; thus they discovered the Electro-type process.

Jacobi's process is as follows:

1. *Apparatus.*

A. For small objects:—The object to be copied (for shortness we shall call it the *Model*)—which must be a conductor, at least on its surface—is immersed in a solution of sulphate of copper, and made to form the negative conductor of a galvanic circuit, the positive conductor consisting of zinc immersed in dilute sulphuric acid, sal-ammoniac, common salt, or sulphate of soda. The most suitable apparatus is an oblong box of wood (pitched with asphalt), or porcelain, divided into two parts by an upright partition of slightly baked unglazed earthenware (or else of elm-wood which has been boiled for an hour in water acidulated with sulphuric acid). The division containing the copper is filled with solution of sulphate of copper saturated while hot, and is fitted at its upper part with a thin wooden box perforated at the sides and bottom and filled with pounded sulphate of copper, for the purpose of keeping the solution constantly saturated. The zinc division contains dilute sulphuric acid, or a solution of sal-ammoniac, &c., together with a zinc plate, which—at least when sulphuric acid is used—must be amalgamated. For renewing the liquids, especially of the zinc division, each division has an opening at the side, communicating first with a flexible tube of caoutchouc, and then with a rigid tube, which, when set upright, reaches to the top of the vessel, but when let down allows the liquid to escape. The zinc is connected with the model by means of a wire, under which a magnetic needle is placed; and the model is immersed upright in the copper division, with the side which is to be coppered turned towards the zinc division. The deflection of the needle indicates the quantity of the current, on the regulation of which the success of the operation greatly depends. When the quantity of electricity is too great, the sulphate of copper is decomposed more quickly than fresh sulphate is dissolved, and the copper deposited on the model no longer exhibits the bright red colour which it ought to possess, but becomes of a dirty brown red, and loses its coherence; and even if the solution be then saturated, the precipitate afterwards deposited is still incoherent: the brown-red precipitate must, therefore, be scraped off or removed by nitric acid. As soon, therefore, as the magnetic needle indicates that the current is too strong, it must be weakened by diluting the acid, increasing the distance between the plates, or by using a connecting wire of greater length and less thickness. The greater the size of the box containing the sulphate of copper, and the more the solution of that salt is accelerated by raising the temperature, the greater may be the strength of the current, and the more quickly will the thickness of

the coating increase; but the more slowly the copper is reduced, the greater will be its compactness and solidity.—Instead of the box above mentioned, a cylinder may be used, having an earthen vessel dipping into its upper part. The zinc plate is placed horizontally on supports in the lower vessel, the model in the upper one—or *vice versâ*,—but the latter arrangement is not so convenient.—The earthenware diaphragm becomes gradually stopped up, and must, therefore, be occasionally soaked in water.

B. When larger objects are to be copied, the current of a single pair of Daniell's constant battery is preferable. The arrangement of the apparatus is that of Jacobi (p. 422). Since it is difficult to obtain large earthenware cylinders, a number of small batteries may be united,—*e. g.*, nine cylinders of copper or lead may be placed in a leaden trough containing solution of sulphate of copper, an earthenware cylinder filled with acid immersed in each of them, and a zinc cylinder made to dip into the acid; all the zinc cylinders being connected by one thick wire, and all the lead or copper cylinders by another. The electricity of these two wires is carried over to the decomposing cell, which at the beginning is filled with dilute solution of sulphate of copper, containing a little free acid. The model lies horizontally at the bottom of the cell, with the side to be coppered turned upwards. A wooden frame is let down to the middle of the liquid, and a piece of linen or flannel stretched over it. Above this diaphragm is placed a plate of copper, or a number of pieces of copper in immediate contact with one another. This copper is connected with the copper or lead of the battery, whilst the model is connected by a wire with the zinc of the battery. As fast as copper is deposited upon the model, the copper forming the anode dissolves (p. 463). At the same time it often becomes covered with a dark red powder, which, if it fell upon the model, would render the copper reduced upon it brittle. This is prevented by the linen. The model must be at least from half an inch to two inches below the copper—for large objects, three or four inches. In this case, also, it is necessary to allow the current to act upon a magnetic needle, in order that some idea may be formed of its quantity. If the Daniell's battery consists of several pairs, a number of decomposing cells may also be included in the circuit.

2. *Constitution of the Model.* The model is either a conductor or a non-conductor covered with a thin layer of a conducting substance.

A. Every metal may be used which does not by itself precipitate copper from the solution of the sulphate—even lead, which, though it precipitates the copper slowly at first, ceases to do so as soon as its surface is covered with that metal. Tin, which exerts a stronger chemical action on the solution, and is itself dissolved at the same time, does not yield impressions of equal sharpness. The noble metals, copper, type-metal (lead and antimony), and fusible metal (2 parts bismuth, 1 tin, and 1 lead), are peculiarly well adapted for the purpose; brass, on the contrary, is not,—because the reduced copper is not easily separated from it, and when separated is found to be coated with a film of brass. When the copper is reduced on an engraved copper plate the separation is easily effected, provided the lines are not too deeply engraved or under-cut,—and the engraved plate is not spongy, porous, or lamellated on the surface, has no blemishes, as they are called,—and the newly formed plate is of a proper thickness. When these conditions are fulfilled, the reduced plate separates almost spontaneously as soon as the edges are filed away. The plate to be engraved is best formed by galvanic action, inasmuch as the

reduction of copper on a plate previously ground and polished takes place with extreme slowness. Such a plate requires no grinding or polishing; and, in consequence of its homogeneity, the copper reduced on its surface after engraving may be easily separated. Since, on ordinary copper plates, the adhesion on some parts of the surface is so strong that the separation cannot be effected without injury to the original, it is necessary, before commencing the process of reduction, to cover the engraved plate with an extremely thin layer of grease. For example, it may be covered with melted stearic acid, which separates completely after cooling, but leaves a trace of grease (probably oleic acid), in a very finely divided state, on the plate of copper. The subsequent separation of the reduced copper is also greatly facilitated by silvering or gilding the engraved plate before commencing the electro-type process. Gilding in the wet way is best adapted for the purpose. Pieces of copper stamped with the die may also be used as models, provided they are not underworked. Further, if an engraved copper plate be pressed under a rolling press on a leaden plate, copper may be reduced on the latter by the electrotype process, and perfectly sharp, exact copies thus obtained.—The parts of the model which are not to be covered with copper are previously coated with wax; so likewise is the conducting wire, so far, at least, as it dips into the solution.

B. The non-conductors used as models, are wood, gypsum, porcelain, sulphur, sealing-wax, stearic acid [this appears to be what Jacobi means by stearine]. Gypsum must be soaked in a hot mixture of stearic acid and wax, till it no longer gives out air-bubbles. Casts of stearic acid are much sharper than those of gypsum. To give these models a conducting surface, a quantity of plumbago is rubbed up with the water to a semifluid consistence, and spread, by means of a brush, on those parts of the model which are to be coppered; after drying, the superfluous plumbago is rubbed off with a dry brush. Or the plumbago, in the state of dry powder, may be rubbed on the model with a brush slightly moistened with oil. Since the coating of plumbago conducts but imperfectly, the deposition of copper is most abundant at the point where the plumbago touches the conducting wire. It is therefore advantageous to place a thin strip of lead or copper, connected with the conducting wire, close round the surface to be coppered. The metal must also be placed in a horizontal position.—When a great degree of malleability is not desired, the growth of the layer of copper, when it has once begun to form, may be accelerated by strewing copper filings on it, which become intimately mixed with the reduced copper.

The electro-type process is applicable to copper-plate engravings, medals, stereotype plates, ornaments,—and likewise to making blocks for printing calico and patterns for paper-hanging. (Jacobi.)

Methods of others.

Apparatus and Liquids.

Spencer's Apparatus. A cylinder of glass, wood, or glazed earthenware (having a rim at the bottom for retaining the gypsum), is closed at the lower end with a diaphragm three quarters of an inch thick. It contains zinc immersed in a solution of common salt, and is itself surrounded by a solution of sulphate of copper, which contains the body to be coppered. The operation succeeds best when the surface to be cop-

pered is of the same size as the zinc surface, and that of the gypsum greater than either. The zinc is frequently cleansed, the salt-solution occasionally renewed. When the process is continued for some time, the copper solution must likewise be renewed; otherwise the sulphuric acid which is set free prevents the precipitated copper from assuming a solid consistence, and converts it into a brown-red powder; in such a case, the copper must be cleaned with very dilute nitric acid. The formation of a layer of copper one-eighth of an inch thick, takes eight or ten days. (Spencer.)

Böttger's Apparatus. A cylinder six inches high (*e. g.* a lamp-glass), open at top, and tied round at bottom with a thin piece of bladder, is sunk to one-half its depth in a somewhat wider cylinder, and fixed in this position by means of three fork-shaped ignited copper wires. In the lower cylinder, two and a-half or thee inches from the bladder, is placed a ring of unignited copper wire. The model is laid upon a ring of unignited copper wire, placed in the lower cylinder at the distance of two and a-half or three inches from the bladder, and terminating in a wire which passes up the side of the lower cylinder—then down the inner surface of the upper cylinder to within three lines' distance from the bladder—and there forms a ring, on which the zinc plate is laid. The whole surface of the copper wire in the lower cylinder, with the exception of the ring, is covered with sealing-wax, to prevent unnecessary precipitation of copper. The lower cylinder is filled with solution of sulphate of copper, saturated in the cold (which need not be pure, and may contain a large quantity of sulphate of zinc), and contains some crystals of the same salt. The upper cylinder contains a thick plate of zinc, partially amalgamated and of the same width as the cylinder, together with a mixture of 1 part of oil of vitriol and 10 parts of water. It is immersed to the depth of an inch or two in the solution of sulphate of copper.—Every twenty-four hours, the upper cylinder together with the wire is taken out of the lower vessel, the copper solution in the latter stirred up, and supplied, if necessary, with fresh crystals (or it is saturated every two days with sulphate of copper at a boiling heat, and filtered through linen when cold): the acid is also changed, and the zinc plate cleaned or renewed. In the course of a week, a deposit, one or two lines in thickness, is obtained. (R. Böttger, *Ann. Pharm.* 35, 216.)

In Jacobi's apparatus A, the deposit of copper is more uniform and pure, when the model is placed upright, than when it lies in a horizontal position. It is not only when the solution of sulphate of copper is too weak, that the metal is deposited in a pulverized state, but likewise when the surface on which it is deposited is too small in proportion to that of the zinc. Two or three models may be immersed in the copper solution at the same time. If the copy, after separation from the model, be immersed for a short time in the copper solution, the zinc connected with it remaining at the same time in the acid, the copper thus deposited on the surface of the impression gives it a beautiful soft silky lustre. (Solly.)

In Jacobi's apparatus A, the copper wire attached to the zinc must be amalgamated, as far as it dips into the solution, to prevent the evolution of hydrogen gas upon it, by which part of the action would be lost. (Bolley, *Ann. Pharm.* 37, 206.)—Boquillon's apparatus. (*J. Pharm.* 27, 216.)

Smee (*Phil. Mag. J.* 16, 550) prefers Jacobi's apparatus B to the simple galvanic circuit A. He however uses in connexion with it a trough battery containing from two to six pairs. Along the bottom of

the decomposing cell filled with sulphate of copper, there runs a wire, on which are placed as many models as may be desired; and these can be taken out separately and replaced by new ones, without disturbing the rest. The positive wire passes over to a large piece of copper, which dips into the copper solution. From nitrate of copper, the metal is deposited more quickly but in a more brittle condition, than from the sulphate.—Jordan (*Phil. Mag. J.* 19, 452) also prefers apparatus B.

In order to neutralize the free sulphuric acid which accumulates in the copper solution, and at the same time to keep the liquid saturated with sulphate of copper, small bags filled with oxide of copper are suspended in the solution.—The coating of copper is thickest exactly at the point which is farthest from the conducting wire, whether the model be placed upright or horizontally,—and in the former case, whether the conducting wire be attached to the upper or lower end of the model. For this reason, it is necessary either to have two conducting wires fixed on opposite sides—or, if a single wire be used, to change its point of attachment from time to time. Sometimes streaky deposits of copper are produced on the further side of the model, even when the current is very feeble. (Gerlach, *J. pr. Chem.* 24, 180.)

Engraved Copper-plates. An engraved copper-plate is carefully rubbed with olive-oil, then cleaned and put into the apparatus already described (p. 505),—which must, however, be of larger dimensions, and in which the plate is four inches distant from the bladder. After ten days, the double plate is taken out and fixed in a vice, and the edges filed all round, till the boundary line between the copy and the original becomes apparent; the blade of a pocket-knife is then carefully inserted between them, a thin horn spatula introduced into the split thus made, and by means of this the plates are completely separated. The reversed copy thus obtained, of the thickness of half a line, is cleaned with caustic potash, then rubbed with olive oil, and the oil removed with very soft blotting-paper, with the assistance of a brush. The reversed copy is then subjected, in the same manner, to the galvanic process for fourteen days; another copy is thus obtained, easily separable, similar in every respect to the original plate, and giving perfectly similar impressions. Böttger succeeded perfectly in this process with a plate twelve inches high and nine inches wide. (*Pogg.* 54, 300; also *J. pr. Chem.* 25, 116.)

In order that the reduced copper may separate with facility from the original plate, the latter is previously rubbed, while warm, with yellow wax mixed with a small quantity of turpentine, and the wax wiped clean off after the plate has cooled. When the precipitation of the copper is complete, the back of the reduced plate is heated over a spirit-lamp; it then separates spontaneously with a decrepitating noise. The plate thus obtained is then treated with wax in the same manner,—and so on. (Spencer.)—Max, Duke of Leuchtenberg, rubs melted stearic acid into the plate, and wipes it off again with linen.

Since the rubbing in of grease into the plate may obliterate the lines, the process of silvering (recommended by Jacobi) is to be preferred. The plate is dipped, for ten minutes, into a solution of chloride of silver in common salt, and when thus slightly silvered—the atoms of copper on the surface being replaced by silver—it is introduced into an apparatus like that of Böttger. Instead of a ring of copper wire, however, the plate is supported on a broad sheet of copper, on which a narrower vertical sheet is soldered. This broad sheet of copper—which is entirely covered

with wax, with the exception of a space about half an inch wide all round the plate which lies upon it—prevents the deposition of copper over the edge of the original plate. The strip of copper passing upwards is screwed to a strip of lead, which lies upon the zinc plate and is kept upon it by means of weights. This arrangement facilitates the cleaning of the zinc plate. The reversed plate is finished in six or eight days. A plate, similar to the original, is prepared from it in a similar manner. (Kobell, *Polytechn. J.* 77, 68; *Allg. Zeit.* 1842, No. 54 Beil.; *comp.* Max Herz. *v.* Leuchtenberg, *J. pr. Chem.* 23, 143.)

An engraved copy may be obtained from a smooth copper plate, by drawing on the plate with thick varnish, and then coating it with copper by means of the battery. The copy thus obtained may be used to print from; but the depressions are shallow, and do not retain the ink well. (Smee.)—The drawing is best made with a solution of common resin in oil of turpentine, mixed with Venetian red, mineral black, and other mineral colours. When this ink has been put on, the plate is silvered in the manner already described, and then treated by the electrotype process. The copper is deposited on the ink as well as on the uncovered portions of the surface, partly because the copper underneath acts through the ink, and partly by gradual growth from the side. From the plate thus obtained a reversed copy is made, and from this copies similar to the original may be obtained, as many as may be desired. (Kobell, *Allg. Zeit.* 1842, No. 54; *Pogg.* 54, 303).

To obtain a copper-plate with raised lines fit for printing, a flat plate is covered with a coat of wax, and the lines etched upon it. The exposed part of the copper is then subjected, for a short time, to the action of nitric acid diluted with three parts of water (without this previous treatment with acid, the deposited copper would not adhere firmly. The plate is then submitted to the electrotype process, the reduced copper ground smooth with pumice-stone, and the wax removed by warming and rubbing with turpentine.—Or an engraving is made on lead or type-metal—all the lines being of equal depth and flat at the bottom—and from this an electro-type copper plate is formed, which may be used for printing. (Spencer.)

Metallic Models. The best material for taking impressions is an alloy of 8 parts bismuth, 8 of lead, and 3 of tin, which melts at 107·5° C., or 225·5° Fah. (Rose's fusible metal produces a coarse-grained mass on cooling, and does not give equally sharp impressions.) This alloy is fused, poured into a perfectly dry pasteboard tray, at least three lines in depth, stirred with a hot iron rod till its surface is free from oxide and air-bubbles, and left to cool to a semifluid consistence. The medal or coin is then heated till it can scarcely be held in the hand, then quickly laid on the alloy, and pressed firmly and continuously on it by means of a broad cork fastened to a handle, till the mass has become tolerably cool. (R. Böttger.)

Impressions of steel and copper engravings may be taken with Rose's fusible metal, by placing the alloy, just as it begins to cool, under a vertically acting press, and leaving it there till it is cold. The electro-type plate formed upon this alloy is easily separated.—If the copper is to be precipitated on the original plate, the latter must be well rubbed with oil, and then carefully cleansed, these operations being repeated several times. (Marchand, *J. pr. Chem.* 23, 466.)

If casts of silver and gold objects be made in fusible metal, the copper reduced upon them has a white or yellow tint on its surface. (Solly.)

Good casts may also be made with melted lead, as recommended by Spencer; but the normal plates, when rather thin, become oxidated and distorted by the heat which this metal requires to fuse it.

A plate of lead, which must be perfectly clean, may also be laid on the engraved copper plate and subjected to the action of a very powerful press. For medals, which may be placed between two plates of lead, a vice is sufficient. Impressions even of wood-cuts may be taken in lead. For this purpose rolled lead must be used, not cast lead, which is more solid. The impressions are very sharp. When the copper has been reduced upon the lead, it may be separated in a few seconds by heating the hinder surface over a spirit-lamp, the separation being effected by the difference of expansion of the two metals. (Spencer.)

Böttger lays upon the medal thin sheet lead, freed from grease by means of caustic potash, surrounds the whole with well-moistened pasteboard, and submits it to the pressure of a vice, a press, or a heavy hammer. To keep the lead plate from bending, it is fastened with wax at three points to a thicker lead plate, and then subjected to the electrotype process. Separation is easily effected.

Non-conducting Models. Stearic acid, spermaceti, wax, colophony, isinglass, &c. serve for seals and gems which do not sustain a high temperature. Finely pounded plumbago is rubbed in with cotton or laid on with a brush; the impression is however not so sharp as when a metallic alloy is used. (Böttger.)

To give a conducting surface to plaster casts, paste models of gems, earthenware articles, wood-cuts, &c. Spencer (*Pogg.* 51, 376) wets them with silver solution, and exposes them under a bell-jar to the vapour of a solution of phosphorus in alcohol, ether, or oil of turpentine, contained in a watch-glass placed upon warm sand. Reduction takes place in two minutes. Porous objects may likewise be moistened with gold solution, and the gold reduced by sulphurous acid gas. (Spencer.)—The reduction of silver in this manner is however tedious and irregular. Böttger therefore (*Ann. Pharm.* 39, 180) recommends the process of heating a few grains of phosphorus with alcohol and a small quantity of potash, and admitting the non-inflammable phosphuretted hydrogen gas thus evolved into the space in which the plaster cast, saturated with solution of silver and still moist, is situated. Reduction takes place instantly.—Elsner (*J. pr. Chem.* 22, 346) mixes up finely powdered gypsum with filtered sour whey instead of water. The cast thus obtained is covered, after drying, with solution of silver and exposed to sunlight; it then assumes a brown colour from reduced silver, and is well adapted for the deposition of copper.

To obtain casts of figures, the figure formed of stearic acid is covered with plumbago and coppered in Jacobi's apparatus B. The stearic acid is then melted out, a bladder containing zinc and dilute sulphuric acid suspended in the hollow, the remaining space filled with solution of sulphate of copper, and the zinc connected with the copper mould. After a few days, the outer mould may be separated from the cast formed within it. (Max. Herzog von Leuchtenberg, *J. pr. Chem.* 23, 146.)

Since copper obtained by the electrotype process soon tarnishes on exposure to the air, becoming sometimes yellow, sometimes red, Solly recommends that it be heated to redness, whereby it will acquire a uniform and permanent grey tint, and when slowly cooled will be perfectly ductile.—Copper precipitated by galvanic action breaks, on being bent, at the same angle as cast copper; but after being ignited and slowly cooled,

it is as flexible as sheet copper. [Spencer).—Copper obtained by galvanic action is very hard and brittle, even when it has been precipitated by a very feeble electric current. By ignition it becomes perfectly soft and malleable, but at the same time it undergoes considerable expansion, so that a strip of galvanic copper $5\frac{1}{2}$ inches long is lengthened a quarter of an inch after ignition and cooling, an expansion which amounts to $\frac{1}{22}$ of its length. Hence the copy of an engraved plate must not be ignited, particularly as the expansion might be unequal in different directions, and a distorted picture would consequently be produced: another objection is that the greater softness of the ignited copper would diminish the number of impressions that could be taken from it. But if the plate be heated only to the temperature of melting zinc (about 227° C. or 400° F.) it will not be injured, but merely so far deprived of its brittleness as not to break under the press. (Gerlach.)

To obtain electrotype impressions and copper plate engravings from a Daguerréotype picture (p. 178), the following process is adopted. The plate on which the sun-picture is formed, is covered on the back and edges with shellac varnish, with the exception of one spot on the edge to which the conducting wire is afterwards to be attached. The same treatment is applied to a platinum plate of equal size, which is coated with pulverized platinum by Smee's method (p. 419), in order that the hydrogen gas may be more easily evolved and not accumulate in large bubbles; for this would weaken the galvanic action on the opposite part of the sun-picture. The two plates are disposed parallel to one another and two inches apart, in two grooves of a wooden frame,—and, together with this frame, dipped vertically into a mixture of two measures of hydrochloric acid and one measure of water (sp. gr. 1·1). The electric current, which acts upon these two plates—of which the Daguerréotype plate plays the part of anode and the platinum plate that of cathode—is produced by a single pair of Grove's battery—zinc, dilute sulphuric acid, concentrated nitric acid, and platinum (p. 422). The zinc and platinum plates of the battery must be of the same size as the Daguerréotype plate. The circuit is closed by means of two platinum wires. The platinum wire, proceeding from the platinum plate of the exciting cell, is pressed upon that point of the sun-picture which is not covered with shellac-varnish, and the wire proceeding from the zinc plate simultaneously pressed upon the uncovered spot of the platinum plate, an assistant noting the time. The action is completed in an interval of time varying from twenty-five to thirty seconds (with other galvanic apparatus the time would be different). The frame is therefore taken out after twenty-five seconds, the plate washed with pure water, and if the action is not found to be quite complete, again submitted for a few seconds to the electric current. The plate, after being washed, is laid in a flat box containing very dilute solution of ammonia,—the picture, which is of a brown colour, being turned upwards—and the picture gently rubbed with soft cotton till all the precipitate is dissolved. The plate is then immediately taken out, washed, and dried.

The best mode of using a plate thus treated, is to take electrotype copies from it; any required number may be obtained, and all very exact. For printing, the plate is not so well adapted; for if it be so slightly etched with hydrochloric acid as not to obliterate the finer touches, the printing ink will not hold well in them, and the impressions obtained will be imperfect; and if the acid has acted more strongly, the ink adheres well, it is true, but the finer traits of the sun-picture are destroyed. —A Daguerréotype plate may indeed be directly treated by the electro-

type process without previously subjecting it to the action of hydrochloric acid in the electric circuit; but such treatment yields only a single very faint impression,—and in taking this, the original is destroyed. (Grove, *Phil. Mag. J.* 19, 247; 20, 24; also *J. pr. Chem.* 25, 291.)

Theory of Galvanism.

1. In 1790, Galvani discovered that the exposed muscles of living animals are thrown into convulsions by contact with different metals, and he endeavoured to explain this phenomenon by assuming the existence of a peculiar kind of electricity, which he called Animal Electricity. Volta ascribed the phenomenon to common electricity, which he supposed to be developed by the contact of dissimilar metals. This he endeavoured to prove by his *Fundamental Experiments*, in 1796. In 1800, he invented the pile called after his name—an instrument to which chemistry was soon indebted for the most important advances. According to Volta's Contact-theory, Galvanism or Galvanic Electricity is produced, not by chemical changes, as has been assumed in the present work (pp. 328...430), but solely in consequence of the contact of dissimilar conducting bodies. On this supposition, Contact-electricity takes the place of Chemical-electricity. The leading principles of Volta's theory are as follows.

When two dissimilar conductors, *e.g.* zinc and copper, touch one another, a very small quantity of positive electricity passes from the copper to the zinc and an equal quantity of negative electricity from the zinc to the copper, until a certain, but always very small electrical tension is attained. In contact with lead, also, zinc takes positive electricity while the lead takes negative electricity, but only up to a much lower degree of intensity. On the contrary, when lead and copper are in contact, the lead takes positive and the copper negative electricity; but in this case also, the intensity is less than in the case of zinc and copper. In accordance with this view, an *Electric Series* or *Series of Intensity* of conductors may be drawn up, proceeding, according to Volta, as follows: Zinc, lead, tin, antimony, brass, copper, platinum, silver, gold, charcoal, graphite, peroxide of manganese. (This series has since undergone several alterations.) Zinc takes positive electricity when in contact with any of the conductors above mentioned, and is therefore the most electro-positive of them all; peroxide of manganese, which takes negative electricity when in contact with any of the metals, is the most electro-negative. The other conductors are electro-positive towards all those which follow, and electro-negative towards all which precede them in the series; but the electric tension of two metals is greater, the farther they are removed from one another in the electric series.—Volta likewise supposes that a good conductor excites electricity when in contact with a watery liquid, the metal taking the negative, the liquid the positive electricity.—When two metals, zinc and copper for example, are in contact with one another and also with a watery liquid, the positive electricity accumulated on the zinc, and the negative electricity accumulated on the copper, neutralize one another through the medium of the liquid,—whereupon, positive electricity again passes from the copper to the zinc, and negative electricity from the zinc to the copper. These quantities likewise unite through the medium of the liquid, and thus a constant current is kept up, positive electricity passing from the copper to the zinc, from the zinc to the liquid, and from the liquid to the copper again. The decompositions, which the liquid undergoes during this process, are

not the cause of the electric current as we have hitherto supposed (pp. 341... 345), but a consequence of it.

This theory of contact, to which many of the most distinguished cultivators of physical science are still attached, rests principally on Volta's *Fundamental Experiments*, from which it would appear that in the contact of dissimilar metals, even when no chemically acting liquid is present, electrical tension is developed. But even if the greater number of these experiments are assumed to be correct, they still admit of another interpretation, in accordance with the supposition that chemical action is the cause of the electric tension produced. A few examples will perhaps make this clear. It must previously be stated that in these experiments a gold-leaf or straw-haulm electrometer fitted with a condenser is used. The lower plate of the condenser is screwed on to the electrometer; the upper plate may be removed by an insulating handle. The surfaces of the two plates of the condenser which touch one another, are ground very smooth and covered with a thin coat of varnish.

Exp. 1. Both plates of the condenser consist of zinc. The lower zinc plate is touched with a copper plate held in the hand. If the copper plate be then removed and the upper plate of the condenser subsequently raised, the electrometer shows positive electricity in the lower zinc plate. This plate has therefore taken positive electricity from the copper plate which touched it. [The oxidizing action of the air and of the moisture contained in it, sets negative electricity free in both zinc plates: this negative electricity is carried away from the lower zinc through the copper plate—accumulates with so much the greater intensity in the upper zinc plate—and gives rise to a transference of positive electricity from the hand through the copper to the lower plate.]

Exp. 2. Both plates of the condenser consist of copper. The lower is touched by a zinc plate held in the hand. On subsequently removing the zinc plate and raising the cover of the condenser, the electrometer exhibits negative electricity. Consequently, negative electricity has passed from the zinc to the copper. [Negative electricity accumulates in the zinc which is in contact with the moisture of the hand and of the air; thence it passes through the hand, which is an imperfect conductor, into the lower copper plate, where it accumulates in greater quantity, in consequence of the condensing action of the cover; on the removal of the cover, the accumulation shows itself.

Exp. 3. The condensing plates are made of copper. A zinc plate is soldered to a copper plate, and the lower plate of the condenser is touched by the copper plate, while the zinc plate is held in the hand. After the separation of the copper plate and cover, negative electricity shows itself in the lower plate. [The same explanation as in Exp. 2.]

Exp. 4. The same arrangements as in Exp. 3. The copper plate is held in the hand, and the lower plate of the condenser touched by the zinc plate, not directly, but with the interposition of a piece of moistened paper. On removing the zinc plate and cover, the electrometer shows positive electricity. [In consequence of the action of the liquid in the paper on the zinc, negative electricity accumulates in the zinc, and positive electricity in the liquid; the positive electricity is consequently communicated to the plate of the condenser.]

That zinc and other metals oxidate in the air at common temperatures is proved by their tarnishing; even gold and platinum become slightly tarnished. An extremely slight degree of oxidation is sufficient to give evident signs of electricity. (This is likewise shown by Faraday's expe-

riment, p. 376.) Moreover, a certain time is always required for charging the condenser; the transference of electricity is not momentary. A thin layer of varnish does not protect the zinc perfectly,—it allows air to pass through; but the thicker the coating, the more does the development of electricity diminish, finally ceasing altogether. (De la Rive.)—On the contrary, Fechner remarks that even thickly-varnished zinc plates, to which brass or platinum is soldered, give the same electricity; and that electricity is likewise obtained with gold and graphite, and with silver and gold, but not with gold and platinum, because these two metals are too near to one another in the electric series.

The electrical series of metals corresponds, for the most part, to their different degrees of affinity for oxygen and substances allied to it.

The series varies according to the nature of the liquid (*vid.* pp. 351, 352, 353, 363, 364, 366, 374, and 375), that metal which has the greater tendency to combine with the electro-negative element (oxygen, sulphur, &c.) of the given liquid, always appearing the more positive of the two; and the reversal of the current, which sometimes occurs, always corresponds to the greater tendency which the other metal then acquires to appropriate the oxygen, &c., of the liquid. According to the chemical theory, therefore, the explanation of these phenomena is self-evident; but if we adopt the contact-theory, we are obliged to suppose that different liquids produce various, and often very high electric tensions when in contact with different metals,—and that the tensions thus produced overcome that which exists between the two metals, thus giving the current an unusual direction. But the cause of these differences is by no means obvious.

In all cases in which chemical action is absent, there is either no current or a very feeble and uncertain one, which, as shown by Faraday and De la Rive, may be attributed to a trace of impurity in the liquid or the metals, more especially as the galvanometer used in such experiments is possessed of extraordinary sensibility. Why is it that gold gives no current with platinum in nitric acid, although that acid is a good conductor? —and why does the addition of a drop of hydrochloric acid produce a strong current, making the gold positive? Similarly, platinum gives no current with rhodium in nitric acid, but becomes positive on the addition of hydrochloric acid. Palladium gives no current with platinum in hydrochloric acid, but becomes positive on the addition of nitric acid, &c., &c. (De la Rive.) So likewise iron and platinum in solution of sulphuret of potassium give no current, because neither of them abstracts sulphur from the liquid; but all metals which act in that manner produce a current (p. 373).—Lead in sulphuret of potassium is positive towards platinum when first immersed; but after two minutes, the current ceases entirely, because the lead becomes covered with sulphuret—which, though it conducts the feeblest current, prevents the access of the liquid to the lead. (Faraday.) In all cases, the metal which takes up oxygen or chlorine becomes positive; and when the liquid is of such a nature that neither of the two metals can take from it any element of that class, no current is produced, however well the liquid may conduct.—It is remarkable that no current is produced in any case in which chemical action is absent. Now, according to the contact theory, there must in every such instance be an exact equilibrium between the electric tensions of the metal *a* and the metal *b*, the liquid and the metal *a*, and the liquid and the metal *b*. Thus, the theory requires a special adaptation to each particular case; it is incapable of predicting anything. (Faraday.)

No circuit of three solid conductors, *e. g.*, platinum, zinc, and peroxide

of lead (or any imperfectly conducting mineral), ever produces a current (Faraday); the presence of a decomposible liquid, whose atoms are susceptible of transposition, appears to be indispensable.

But the strongest objection to the theory of contact is to be found in the absurdities which it involves. It is not, as Faraday observes, very easy to understand why the unknown force which causes positive electricity to accumulate in the zinc, and negative electricity in the copper, does not retain these electricities in the metals, but allows them to reunite continually through the medium of the less perfectly conducting liquid, and produce a continuous current. This again seems to imply that the decomposition of the liquid is the primary cause of the current. Whoever does not regard it in this light must, as Faraday has shown, admit the possibility of *Perpetual Motion*. To produce this phenomenon, we only require two metals and a liquid whose elements do not combine with either of them. The self-reverting current, constantly excited by these metals, may, by means of electro-magnetic arrangements, be made to give motion to machinery, without being weakened and ultimately destroyed by this expenditure of force. At the same time it perhaps decomposes the liquid, water for example; and, in order that this liquid may not require renewal, the detonating gas given off may be collected in a vessel containing spongy platinum, where it will recombine and form water, and in that state may flow back again to the metals. And there we have the *Perpetual Motion* complete!

One force calls another into action:—friction-electricity is excited by mechanical force; thermo-electricity is connected with the motion of heat; but contact-electricity proceeds from nothing,—it is, in fact, a creation of force. (Faraday.)

Even supposing it should hereafter be proved that electrical tension is excited by the contact of two dissimilar conductors, and that the contact-theory is *so far* true: still, mere contact in a state of rest will never produce a *continuous* current; such a current can ensue only from *continued* chemical action.—It is urged on the part of the contact-theory that strong chemical action is often accompanied by very feeble currents. The chemical theory explains this fact by pointing to the difference between electro-chemical and pure chemical action, the former of which alone excites a current. The contact-theory regards this distinction as an undemonstrated hypothesis, assumed to meet a particular case. But, according to the chemical theory, the distinction is manifest; for the amount of electro-chemical action is exactly proportional to the quantity of hydrogen gas evolved on the surface of the copper—and the amount of pure or ordinary chemical action, to the quantity evolved on the surface of pure zinc.

It is often objected to the adherents of the chemical theory that they do not sufficiently understand the theory of contact. May it not, on the other hand, be safely asserted that many adherents of the contact-theory have never yet given themselves the trouble to acquire a thorough knowledge of the chemical theory? On no other supposition is it possible to explain their frequent citations of facts, which, in their opinion, ought completely to overturn the chemical theory, when in reality they are in perfect accordance with it;—just as in former days, many philosophers, especially among the Germans, from too great partiality towards the old theory of phlogiston, endeavoured to support it by the most ingenious expositions, without paying sufficient attention to the new antiphlogistic theory.

2. Nobili has endeavoured to reduce galvanic electricity to thermo-electricity, in so far as the metals become unequally heated during the chemical action. This view, which has been especially called in question by Becquerel, does not seem to be generally applicable to the facts of the science

3. Fabroni (*Gilb.* 4, 430; 6, 469) and Parrot first declared themselves, in opposition to Volta, in favour of the chemical theory. Among the different supporters of this theory, however, there exist various shades of opinion. Sir H. Davy admitted the existence of contact-electricity as well as that of chemical electricity. Others ascribe the phenomena of galvanism solely to chemical action. Among these latter, some assume the existence of one or two imponderable substances—the electric fluids. To this class belongs the theory of Becquerel, as well as that proposed in the present work: the latter agrees more closely than any other with the views of Grotthuss.—Others deny the existence of a peculiar electrical matter. This view has been most decidedly advocated by Graham: it supposes that the atoms of a body are brought by chemical action into a peculiar polar state, which is propagated throughout the body, and brings about the electrical phenomena. A full exposition of this theory will be found in *Graham's Elements of Chemistry*, pp. 197—235. De la Rive and Faraday also appear to incline towards this view. De la Rive (*Pogg.* 37, 225) regards affinity and electricity as different manifestations of the same force, which probably consists in this—that every atom has the power of throwing the *ether* into a certain state of vibration. In other respects, many of his explanations of galvanic phenomena approach very closely to those laid down in the present work. In a similar manner, Faraday regards the electric current as only another form of affinity, and the forces usually denominated Electricity and Affinity, as one and the same.

Note on Magnetism.

Experiments which seem to show that magnetism is not wholly without influence on crystallization, and on chemical combination and decomposition—but which stand greatly in need of verification—have been described by the following philosophers: Arnim (*Gilb.* 3, 59; 5, 394; 8, 279); Lüdicke (*Gilb.* 9, 375; 11, 117; 68, 76); Mascmann & Hansteen (*Gilb.* 70, 234); Murray (*Phil. Mag. J.* 18, 383; also *Schw.* 34, 133;—*Ann. Phil.* 19, 120); Schweigger and Döbereiner (*Schw.* 44, 84); Reade (*Ann. Chim. Phys.* 38, 196; also *Kastn. Archiv.* 15, 335); and Zantedeschi (*Bibl. univ.* 43, 22):—also Hunt (*Phil. Mag. J.* 28; 1.)

Opposite results, which seem to show that magnetism exerts no influence of the kind, have, on the other hand, been obtained by Steinhöfer (*Gilb.* 14, 124); Erman (*Gilb.* 26, 139); G. Bischof (*in seinem Lehrb. d. reinen Chemie* 1, 66); Kastner (*Kastn. Arch.* 6, 448); B. M. (*Ann. Phil.* 19, 39); Catullo & Fusinieri (*Brugn. Giorn.* 15, 198); Wetzler (*Schw.* 56, 218); Schweinsberg (*Mag. Pharm.* 31, 17, and 144); Brooke (*Edin. Phil. J.* 13, 8); Dulk (*Kastn. Archiv.* 7, 457) and Erdmann (*Schw.* 56, 24).

Magnetic Condition of all Matter.

¶ Faraday has lately made the important discovery that all liquid and solid substances are subject to magnetic influence.—According to the results obtained by this distinguished philosopher, bodies may be

divided into two great classes—the *Magnetic* and the *Diamagnetic*. The former class includes those bodies which exhibit the well known phenomena of ordinary magnetic attraction and repulsion,—being *attracted*, when in their natural state, by either pole of a magnet,—and, when shaped into bars or rods and suspended between two opposite magnetic poles—pointing *axially*, that is to say, in a straight line between them. The bodies belonging to this class are all metallic (including oxides and salts), viz., iron, nickel, cobalt, manganese, chromium, cerium, titanium, palladium, platinum, osmium.—The magnetic properties of iron, nickel, and cobalt have long been known. In the other metals of the series, magnetic susceptibility can only be detected by the use of magnets of great power. Manganese, chromium, cerium, titanium, and osmium, are placed by Faraday in the magnetic class, because certain of their compounds exhibit the ordinary magnetic relations.

The second or *Diamagnetic* class includes all liquids and solids, both organic and inorganic, which do not belong to the *magnetic* class. The law which governs the action of magnets on these bodies is as follows.—*A particle of a diamagnetic body placed in the neighbourhood of either pole of a magnet is* REPELLED *by that pole.*—Hence it follows, that a bar of any diamagnetic substance, suspended by its centre midway between two magnetic poles will point *equatorially*, that is to say, at right angles to the straight line joining the two poles—that being the position in which every part of it is at the greatest possible distance from each of the poles;—and if its centre be placed on either side of the axial line, the whole bar will recede from that line, placing itself at the same time equatorially. A globe or cube does not *point*, but exhibits the simple phenomenon of repulsion.—If two small balls of any diamagnetic substance be suspended between the two magnetic poles, they will be driven towards one another, as if they were actuated by mutual attraction.—The position which a bar of any substance takes up when suspended horizontally between two magnetic poles furnishes the best means of determining whether it belongs to the magnetic or the diamagnetic class;—if it be magnetic, it will place itself axially; if diamagnetic, equatorially.

The diamagnetic force cannot be perceptibly developed without the use of exceedingly powerful magnets: electro-magnets answer the purpose best; but large permanent magnets may also be used. The great power required to develop this mode of action explains the reason of its having been previously overlooked.

Bismuth appears to be the most powerfully diamagnetic of all substances; then follows phosphorus, then antimony, then heavy glass (silico-borate of lead).—Among the metals, the order of diamagnetic energy appears to be as follows: Bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, arsenic, uranim, rhodium, iridium, tungsten.

Some remarkable results are obtained when solutions of magnetic liquids in sealed tubes are suspended in vessels filled with solutions of similar nature, but different strength, and placed between the magnetic poles. For instance, protosulphate of iron is a magnetic substance, being attracted by the magnet, and pointing axially between the poles. Now, water being a diamagnetic liquid, it is possible, by varying the strength of an aqueous solution of protosulphate of iron, to make it either magnetic, indifferent, or diamagnetic, when suspended in air. Suppose, then, two solutions of this salt to be prepared of different strengths, but such as to be both magnetic in air. Let one of these solutions be put into a glass

tube, and the other into a jar within which the tube is to be suspended,—the opposite poles of a powerful electro-magnet being placed on either side of the jar. Then, if the tube be suspended horizontally, with its centre midway between the poles, it will place itself in the axial or equatorial position, accordingly as the solution which it contains is stronger or weaker than that in the jar;—and if it be suspended vertically near to one of the poles, it will be attracted in the former case and repelled in the latter.

These results suggest the consideration whether the magnetic and diamagnetic conditions of matter may not be merely relative,—whether, in fact, all bodies may not be magnetic in different degrees, forming one great series from end to end, with air in the middle. This supposition is considerably strengthened by a review of the magnetic and diamagnetic conditions of gases to be immediately described. A great, if not insuperable, objection to it is, however, that it would oblige us to admit that mere space is magnetic,—since bismuth and all other diamagnetic bodies exhibit the same phenomena in vacuo as in air. Faraday, therefore, inclines to the supposition that diamagnetics have a specific action antithetically distinct from that of ordinary magnetic action. (*Experimental Researches in Electricity*, Series 20 and 21, *Phil. Trans.* 1846, I. 21.)

Air and other gases exhibit decided magnetic and diamagnetic relations. In his first experiments on this subject, Faraday was led to the conclusion that gaseous bodies were indifferent to magnetic action, forming the zero, or middle point, between the two classes of magnetic and diamagnetic bodies. Bancalari has however since discovered that flame possesses diamagnetic properties; and Zantedeschi has shown that air and other gases likewise exhibit diamagnetic relations. The researches of these Italian philosophers have been confirmed and extended by Dr. Faraday: the following are the principal results.

An arrangement was made by which a stream of any gas could be delivered in a vertical direction, either upwards or downwards, near the middle point of the axial line, between two powerful magnetic poles of opposite names, but at a short distance on one side of that line. By this arrangement it was found that the following gases were driven away from the magnetic axis and passed off in the equatorial direction—that is to say—they exhibited diamagnetic relations with regard to atmospheric air: Nitrogen, hydrogen, carbonic acid, carbonic oxide, coal-gas, olefiant gas, sulphurous acid, hydrochloric acid, hydriodic acid, fluoride of silicon, ammonia, chlorine, nitrous oxide, and the vapours of bromine and iodine. Nitric oxide and hyponitric acid were also slightly diamagnetic in air. Oxygen was strongly magnetic—that is to say, it was drawn towards the axis, and then along it in opposite directions towards the two poles, round which it accumulated.

The first mentioned gases evidently differed from each other in diamagnetic energy; but it was found impossible by the means above described to form anything like a precise estimate of their relative powers. To determine this point, the magnetic poles were surrounded with an atmosphere of one gas, while the other gas was directed in a vertical stream, either upwards or downwards, near the axial line as before. By this method it was found that (1) *In carbonic acid gas:* Air and oxygen passed axially; nitrogen, hydrogen, coal gas, olefiant gas, hydrochloric acid, and ammonia, equatorially: so also did carbonic oxide and nitrous oxide,—but the action was feeble. (2). *In coal-gas:* Air appeared magnetic, though but slightly; oxygen was strongly mag-

netic:—nitrogen was strongly diamagnetic; olefiant gas, carbonic oxide, and carbonic acid, feebly so. (3) *In hydrogen gas:* Air, when free from smoke, passed axially; but, when mixed with smoke, it was either indifferent or passed equatorially; hydrogen gas and atmospheric air seem to be not far removed from one another in the scale. Oxygen was strongly magnetic; nitric oxide also magnetic, but in a less degree. Nitrogen was strongly diamagnetic; nitrous oxide, carbonic oxide, carbonic acid, and olefiant gas were also diamagnetic; hydrochloric acid and chlorine slightly so.—Oxygen appears to be the most magnetic (or least diamagnetic) of all gases.

When a spiral of platinum wire was placed just below the middle point of the axial line and ignited by a voltaic current, the stream of hot air which rose up against the axial line was deflected at right angles to the axis, and passed off in the equatorial direction. The same effect was obtained in oxygen, carbonic acid, and coal-gas. Hence it appears that a heated gas is diamagnetic to the same when cold.—A stream of cold air directed downwards near the axial line, was drawn towards that line.

The flame of a wax taper or of burning ether also takes an equatorial direction when placed in or near the middle of the axial line. When placed a little on one side of the axis it is directed away from that line, just as if a gentle wind were blowing upon it in that direction. When made to rise exactly in the axial line, it divides itself into two long tongues, directed at right angles to the axis. This effect is particularly striking with the large flame produced by setting fire to a ball of cotton soaked in ether. These effects are evidently analogous to those just described with hot air; but they are doubtless partly due to the solid carbonaceous particles in the flame, which are known to be diamagnetic. In corroboration of this supposition, it is found that the brightest flames are the most strongly diamagnetic. (Faraday, *Phil. Mag. J.* 31, 401; see also Zantedeschi, *ib.* 31, 421.)

Addendum.

Our knowledge of the Magnetic Forces has lately received the following most important extension. In the Bakerian lecture, delivered before the Royal Society on the 7th of December, 1848, "*On the Crystalline Polarity of Bismuth and other Bodies, and its Relation to the Magnetic Form of Force*,"—Dr. Faraday states, that, in preparing small cylinders of bismuth by casting them in glass tubes, he had often been embarrassed by the anomalous results which they gave, and that having determined to investigate the matter closely, the enquiry ended in a reference of the effects to the crystalline condition of the bismuth, as may be thus briefly stated. If bismuth be crystallized in the ordinary way, and then a crystal or a group of symmetric crystals be selected and suspended in the magnetic field between horizontal poles, it immediately either points in a given direction or vibrates about that position, as a small magnetic needle would do,—and, if disturbed from this position, it returns to it. On resuspending the crystal, so that the horizontal line which is transverse to the magnetic axis shall become the vertical line, the crystal points with its maximum degree of force. If it be again resuspended, so that the line parallel to the magnetic axis be rendered vertical, the crystal loses all directive force. This line of direction, which

tends to place itself parallel to the magnetic axis, the author calls the *Magne-crystallic Axis* of the crystal. It is perpendicular, or nearly so, to the brightest and most perfect of the four cleavage planes of the crystal. It is the same for all crystals of bismuth. Whether this magne-crystallic axis is parallel or transverse to the magnetic axis, the bismuth is in most cases repelled from a single pole or from the stronger of two poles, its diamagnetic relations being in no way affected. If the crystal be broken up, or if it be fused and resolidified, and the metal then subjected to the action of the magnet, the diamagnetic phenomena remain, but the magne-crystallic results disappear, because of the confused and opposing crystalline condition of the various parts. If an ingot of bismuth be broken up, and fragmentary plates selected which are crystallized uniformly throughout, these also point,—the magne-crystallic axis being, as before, perpendicular to the chief plane of cleavage, and the external form, in this respect, of no consequence. The effect takes place when the crystal is surrounded by masses of bismuth, or when it is immersed in water or solution of sulphate of iron, and with as much force apparently as if nothing intervened. The position of the crystal in the magnetic field is affected by the approximation of extra magnets or of soft iron; but the author attributes this result, not to any attractive or repulsive force exerted on the bismuth, but only to the disturbance of the lines of force or resultants of magnetic action, by which they acquire, as it were, new forms. The law of action appears to be that: *the line or axis of magne-crystallic force tends to place itself parallel, or as a tangent, to the magnetic curve or line of magnetic force passing through the place where the crystal is situated.* Hence the crystal changes its direction with any change in these lines. After noticing the magne-crystallic condition of various bodies, the author enters upon a consideration of *the nature of the magne-crystallic force.* In the first place, he examines closely whether a crystal of bismuth has exactly the same amount of repulsion, diamagnetic or otherwise, when presenting its magne-crystallic axis *parallel* or *transverse* to the lines of magnetic force acting upon it. For this purpose, the crystal was suspended either from a torsion balance or as a pendulum thirty feet in length; but whatever the position of the magne-crystallic axis, the amount of repulsion was the same. In other experiments, a vertical axis was constructed of cocoon silk, and the body to be examined was attached at right angles to it, as a radius. A prismatic crystal of sulphate of iron, for instance, whose length was four times its breadth, was fixed on the axis with its length as radius and its magne-crystallic axis horizontal, and therefore as tangent: then, when this crystal was at rest under the torsion force of the axis, an electro-magnetic pole, with a conical termination, was so placed that the axial line of magnetic force should be, when exerted, oblique to both the length and the magne-crystallic axis of the crystal: and the consequence was, that, when the electric current circulated round the magnet, the crystal actually *receded* from the magnet under the influence of the force, which tended to place the magne-crystallic and the magnetic axis parallel. Employing a crystal or a plate of bismuth, that body could be made to *approach* the magnetic pole under the influence of the magne-crystallic force; and this force is so strong as to counteract either the tendency of the magnetic body to approach or of the diamagnetic body to retreat, when it is exerted in the contrary direction. Hence the author concludes that it is neither attraction nor repulsion that causes the set or determines the final position of a magne-crystallic

body. He next considers it as a force dependent upon the crystalline condition of the body, and therefore associated with the original malecular forces of the matter. He shows experimentally that as the magnet can move a crystal, so likewise a crystal can move a magnet. Also that heat takes away the power just before the crystal fuses, and that cooling restores it to its original direction. He next considers whether the effects are due to a force altogether original and inherent in the crystal, or whether that which appears in it is not partly induced by the magnetic and electric forces; and concludes that the force manifested in the magnetic field, which appears by external actions and causes the motion of the mass, is chiefly and almost entirely *induced*, in a manner subject indeed to the crystalline force and additive to it, but at the same time exalting the force and the effects to a degree which they could not have approached without the induction. To this part of the force he applies the word *Magneto-crystallic*, in contradistinction to magne-crystallic, which is employed to express the condition, or quality, or power which belongs essentially to the crystal. In conclusion, Dr. Faraday remarks "how rapidly the knowledge of molecular forces grows upon us, and how strikingly every investigation tends to develop more and more their importance, and their extreme attraction as an object of study. A few years ago, magnetism was to us an occult power, affecting only a few bodies; now it is found to influence all bodies, and to possess the most intimate relations with electricity, heat, chemical action, light, crystallization, and, through it, with the forces concerned in cohesion; and we may, in the present state of things, well feel urged to continue in our labours, encouraged by the hope of bringing it into a bond of union with gravity itself." (*Athenæum*, No. 1103, p. 1266.)

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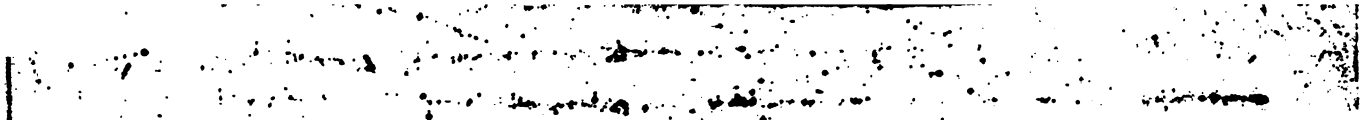

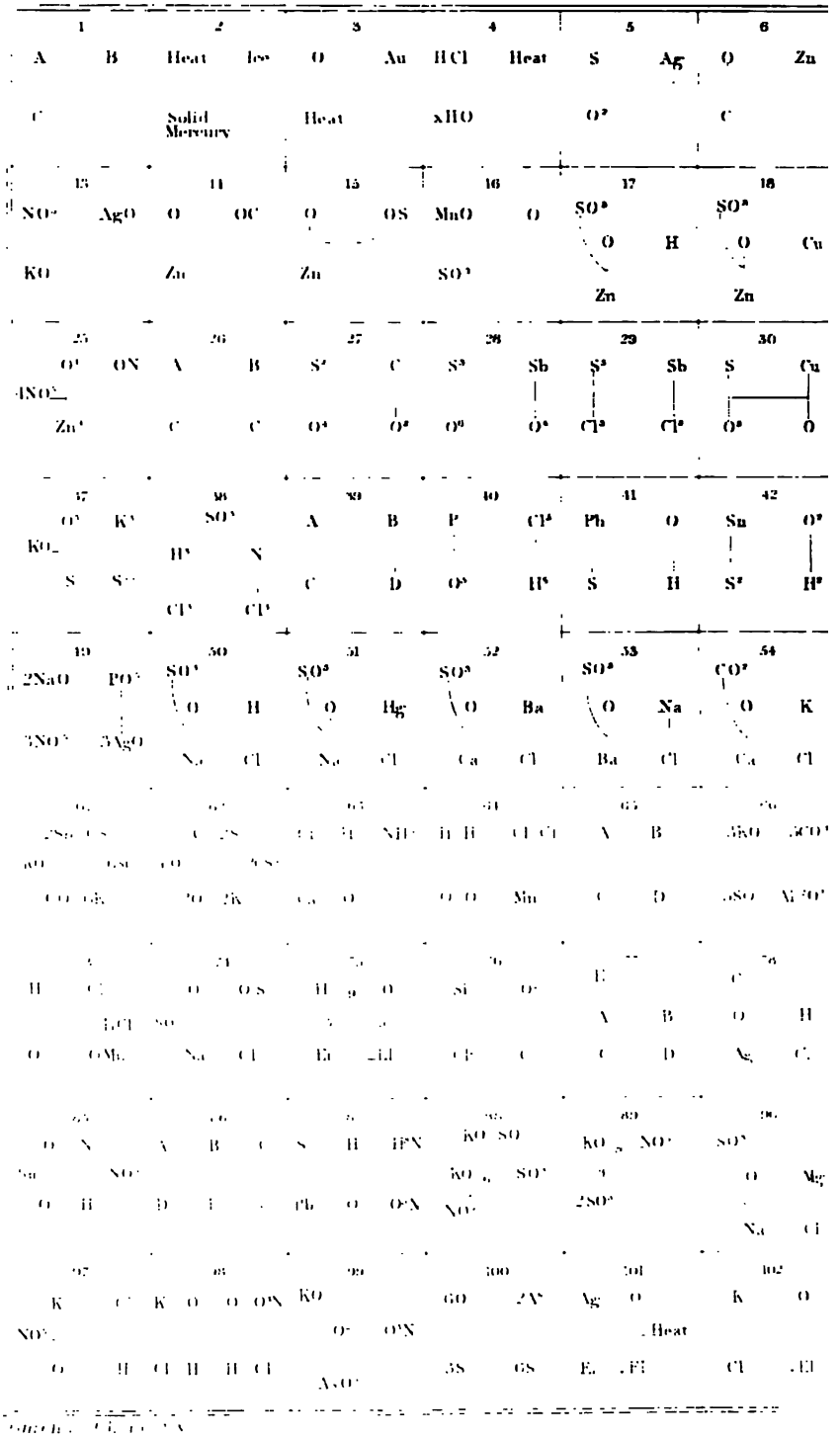

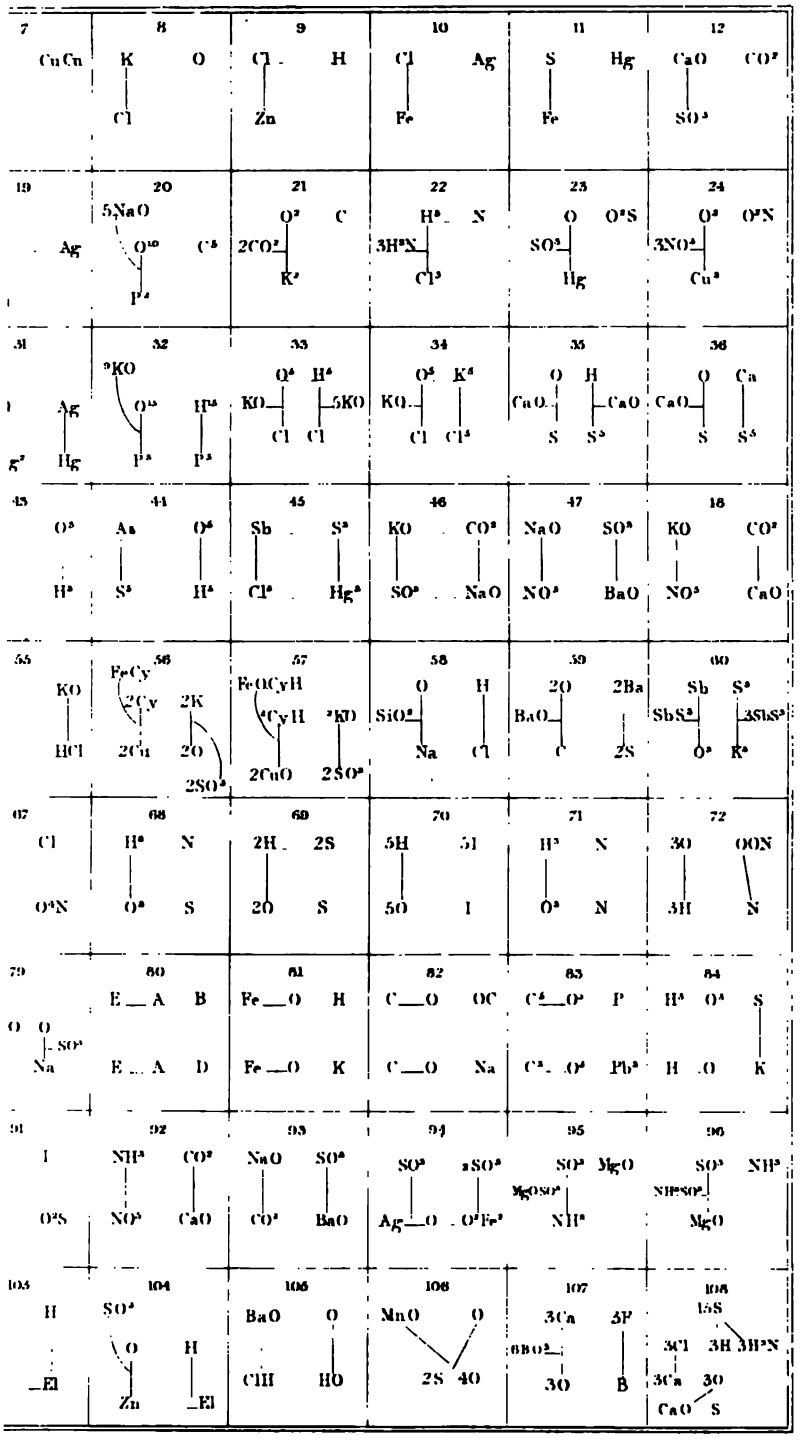
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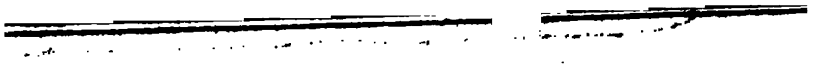

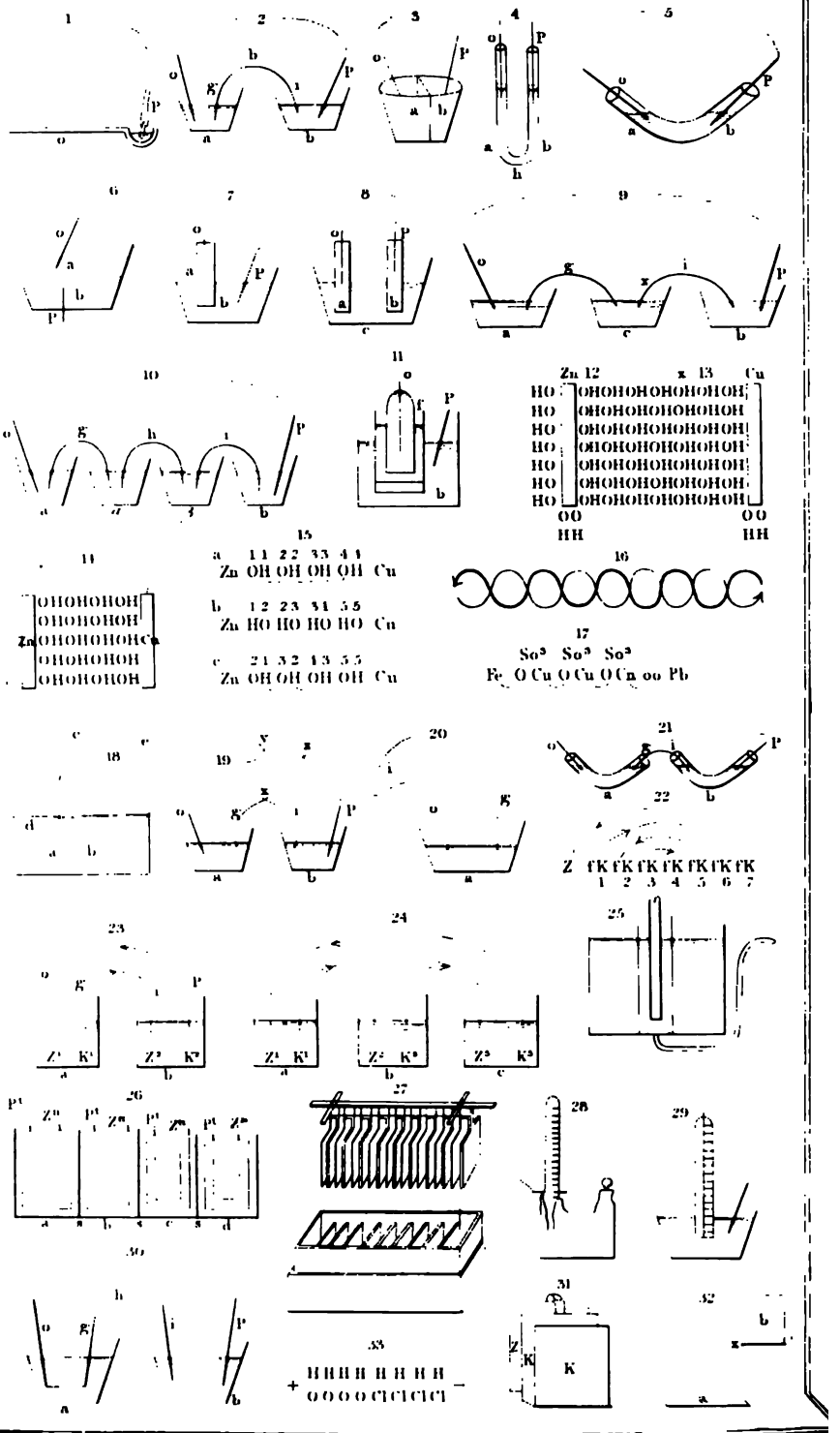
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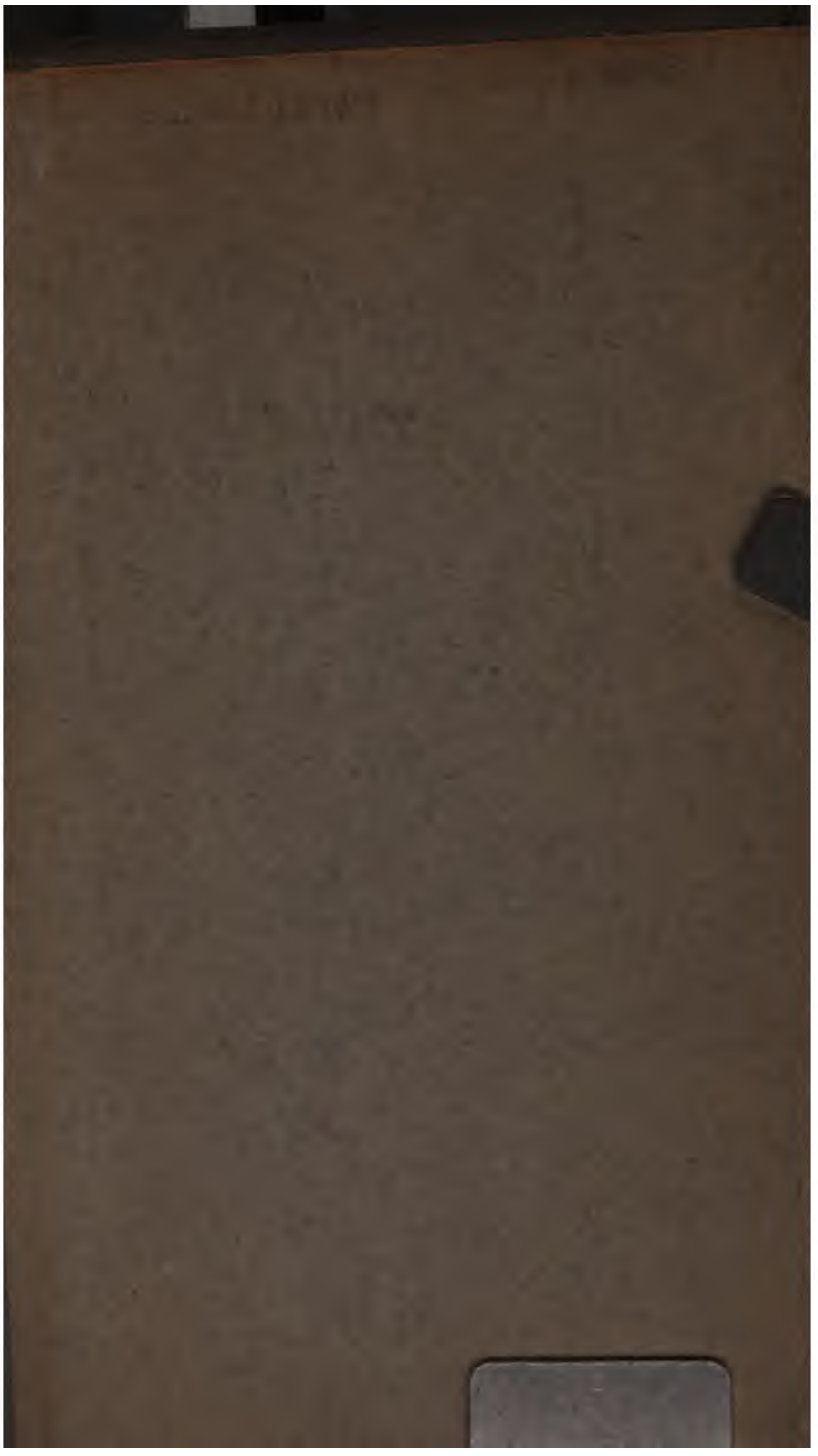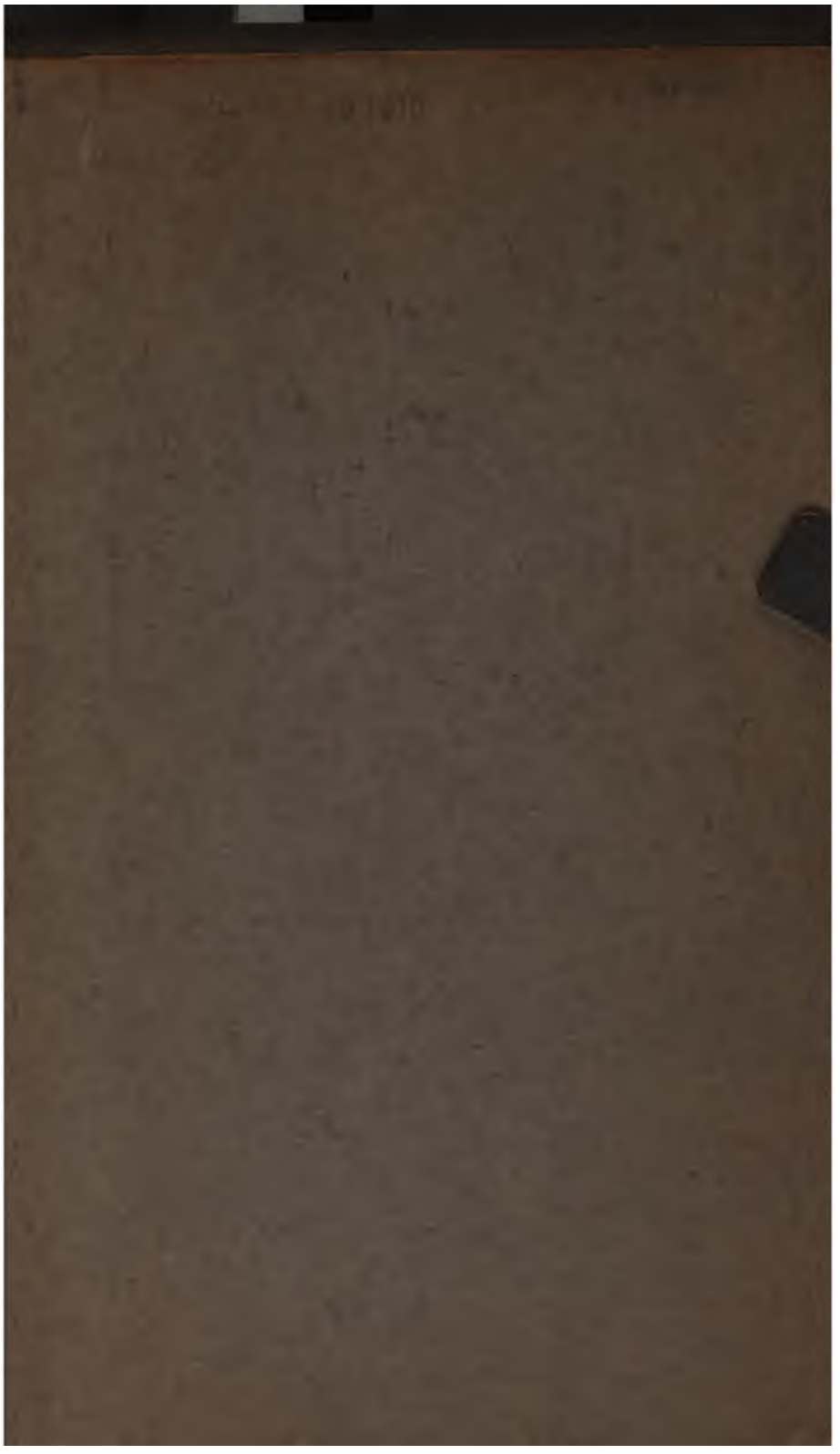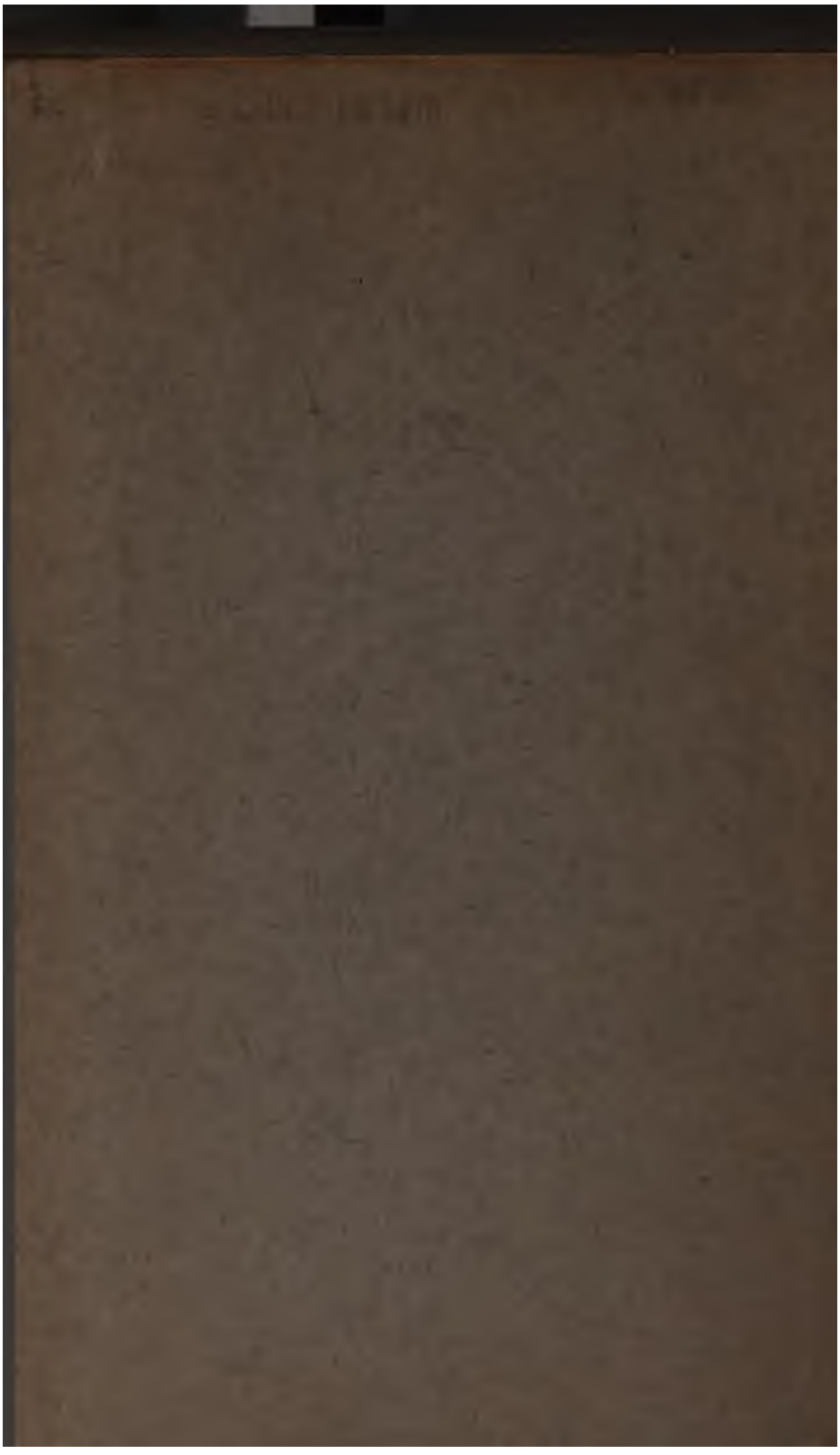
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